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Episodic Acidification and Associated Fish and Benthic Invertebrate Responses in Five Northern Appalachian Streams
An Interim Report of the Episodic Response Project

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EPISODIC ACIDIFICATION AND ASSOCIATED FISH AND BENTHIC INVERTEBRATE RESPONSES IN FIVE NORTHERN APPALACHIAN STREAMS
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by

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and
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The Pennsylvania State University

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This report summarizes progress from October 1988 to May 1989 on an ongoing research project to investigate the chemicals and biological response of five Northern Appalachian Plateau streams to episodic changes in flow . This research described is part of the U.S. EPA Episodic Response Project (ERP), Aquatic Effects Research Program. Research includes monitoring of stream discharge, episodic stream chemistry, precipitation amounts and intensity, and snowpack chemistry and water equivalent. Biological research includes bethic invertebrate surveys, stream bioassays with brook trout and sculpins, and tracking of brook trout movement during episodes using radiotelemetry.

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ABSTRACT

This report summarizes progress from October 1988 to May 1989 on an ongoing research project to investigate the chemical and biological response of five Northern Appalachian Plateau streams to episodic changes in flow. Research described is part of the U.S. EPA's Episodic Response Project, Aquatic Effects Research Program. Research includes monitoring of stream discharge, episodic stream chemistry, precipitation amounts and intensity, and snowpack chemistry and water equivalent. Biological research includes benthic invertebrate surveys, stream bioassays with brook trout (Salvelinus fontinalis) and sculpins (Cottus bairdi and C. cognatus) held in cages during episodes, and tracking of brook trout movement during episodes using radiotelemetry. All streams had median ANC less than 20 microequivalents/L which is typical of Appalachian Plateau basins with sandstone and shale bedrock. Episodic stream chemistry varied considerably among streams with Linn Run and Stone Run routinely exceeding the toxic limit for brook trout of 200 micrograms/L of total dissolved Al and pH less than 5.0 during peak flows. Benner Run and Baldwin Creek did not reach toxic Al levels during episodes, while Roberts Run was intermediate with occasional toxic conditions. In addition, the majority of total dissolved Al was found to be the more-toxic inorganic monomeric Al in all streams. Brook trout and benthic invertebrate population levels indicated variation among streams along an episodic water quality gradient. Bioassay fish mortality occurred commonly during episodes on the more acidic streams. More importantly, radiotelemetry indicated net downstream movement and mortality of adult brook trout during episodes in Linn Run even though some fish found refuge in spring seeps. Fish in Baldwin Creek showed no mortality or net movement during these same events. Episodic monitoring is continuing through Spring 1990 on these five streams with an increased focus on the hydrologic flow paths that cause more severe acidification, episode effects on brook trout reproduction, fish migration during episodes, and the importance of refuges to fish survival.

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INTRODUCTION

Within the National Acidic Deposition Assessment Program (NAPAP), most research that has examined the effects of acidic deposition on aquatic ecosystems has focused on chronic or long-term acidification. However, a number of studies in the United States, Canada and Europe have revealed that significant acidification and water chemistry changes can occur during high flow periods caused by rainstorms and periods of snowmelt. Further, these studies have indicated that these episodes may have significant effects on fish and other aquatic biota. To address concerns regarding the potential of episodic acidification to impact aquatic ecosystems in the northeastern United States, the U.S. Environmental Protection Agency developed the Episodic Response Project (ERP). The major objectives of the ERP are:

(1) Determine the magnitude, duration, and frequency of episodic chemical changes that accompany hydrologic events (both snowmelt and rainstorms) in streams of the United States.

(2) Determine whether episodic chemical changes in streams have long-term impacts on fish populations.

(3) Improve the understanding of processes and factors that influence the severity of episodic chemical changes in streams and their associated effects on fish populations.

(4) Test and develop episodic chemistry models that can be used to make regional predictions of episodic acidification.

Through the cooperation of the Adirondack Lakes Survey Corporation, The Pennsylvania State University, and the U.S. Geological Survey, the ERP initiated field work during the autumn of 1988. Field research will continue through June 1990. However, significant results have been obtained during the first two runoff seasons (Fall 1988 and Spring 1989). So that these results can be included in the NAPAP State of Science and Integrated Assessment reports, each ERP field research group has prepared an interim report (dealing with the first three ERP objectives) that provides a basic presentation of the findings of the first nine months of study. Final reports will be prepared during late 1990 and early 1991 and will include a more in-depth analysis of the ERP data set for the entire study period.

OBJECTIVES AND EXPERIMENTAL DESIGN

Episodic response research on the Northern Appalachian Plateau was conducted by personnel largely from Penn State as part of a larger project also involving groups from the Catskills and Adirondack regions. This report was prepared to generally describe research progress, site characteristics, methods, results and preliminary interpretations of field data collection and data analysis up to June 1989. Data and analysis generally cover the period from October 1988 through June 1989. Objectives of research in the Northern Appalachian Plateau Area were to:

(1) determine the magnitude, duration and frequency of episodic chemical changes that accompany hydrologic events (both snowmelt and rainstorms) in five streams in the Northern Appalachian Plateau (NAP) region;

(2) determine whether episodic chemical changes in NAP streams have long-term impacts on fish and benthic invertebrate populations with specific attention given to:

   a. seasonal changes in community structure and population densities;
   b. spawning effort and reproductive success of the most common species;
   c. mortality rates;
   d. extent of migrations;

(3) improve the understanding of processes and factors that influence the severity of episodic chemical changes in NAP streams and their associated effects on fish and benthic invertebrate populations with specific reference to:

   a. biologically-relevant aluminum chemistry,
   b. flow sources based upon natural isotope tracers,
   c. atmospheric deposition levels.

Research progress will be reviewed with respect to these objectives followed by a site characterization, review of methods and presentation of results covering atmospheric deposition, hydrology, stream chemistry, and biological response research.

Episodic Stream Chemistry - Objective 1

Five stream monitoring sites were established in the NAP region at Linn Run, Baldwin Creek, Stone Run, Roberts Run and Benner Run. Operation began about October 1, 1988 at all sites.

Water sampling during approximately ten events has been completed on each stream. This is in addition to the continuous pH, conductivity, and water temperature monitoring and biweekly baseflow grab sampling. Sites were visited at least weekly to collect data, gage streams, grab stream samples, calibrate probes, etc. Each stream has been gaged by wading with a current meter at least 15 times and rating curves have been developed via regression analysis.

Fish and Benthic Invertebrate Response - Objective 2

Fishery research has involved electrofishing and restocking, "in situ" bioassays and radio telemetry experiments during two intensive data collection periods in Fall 1988 and Spring 1989. A total of seven electrofishing population estimates have been obtained in two 100-m reaches from October 1988 to June 1989 on each stream. Bioassays with brook trout and sculpins were conducted on each stream during each intensive period. Telemetry was conducted on only Linn Run and Baldwin Creek with 10-15 tagged brook trout tracked during each intensive period. Spatial surveys of fish populations at 5-6 locations in each basin outside the 200-m study section have also been conducted in Spring 1989. Benthic macroinvertebrates have been sampled on each stream in Summer 1988, Fall 1988, Winter 1989, Spring 1989 and Summer 1989.

Process-Oriented Research - Objective 3

A precipitation chemistry station was established and operated near the Linn Run and Baldwin Creek catchments beginning in March 1989. Data from a similar MAP3S station monitoring precipitation chemistry on an event basis is also available near State College to serve the Benner, Stone, and Roberts Run sites. Precipitation monitoring stations were also established in November 1988 in the open on each stream basin to record weekly precipitation totals. Snow courses were established on each basin, but little snowfall occurred during Winter 1988-89. Snowmelt lysimeters to monitor snowmelt rates and collect meltwater samples on two basins will be installed by December 1, 1989; one on Baldwin Creek and the other on the Benner Run basin. All these data will be used to relate amount and intensity of rainfall and snowmelt as well as rain and snow melt chemistry to stream episode severity.

Additional water samples were collected for oxygen-18 analysis. Samples were collected from throughfall water, soil water, stream water and groundwater for several selected storms on each basin. Approximately 100 samples have been analyzed to date, but many more have been stored (>600) for possible later analysis. Oxygen-18 analysis will be used to determine water flow paths on each catchment.

In this report standard usage will be that an episode refers to a hydrologic event where ANC or pH decreases. Hydrologic events will be further defined as a streamflow increase due to rain or snowmelt. Acidic episodes will be restricted to episodes in which ANC becomes negative.

RESEARCH SITES

The five research streams and watersheds are described in Table 1 and locations are shown in Figures 1 and 2. All basins are similar in area except for Baldwin Creek which is smaller. These are unglaciated basins underlain by sandstone and some shale bedrock. Soils on the upper part of the basin, which approach 30% slope are sandy loam in texture and extremely rocky. Basins are relatively undisturbed and forested with mixed hardwood trees dominated by oak. Hunting camps are located on all basins except Baldwin Creek. An operating gas well is located on Benner Run and Baldwin Creek basins. A regrowing clearcut area about 10 years old is located on the upper 10% of Benner Run basin and some recent salvage logging of trees killed by gypsy

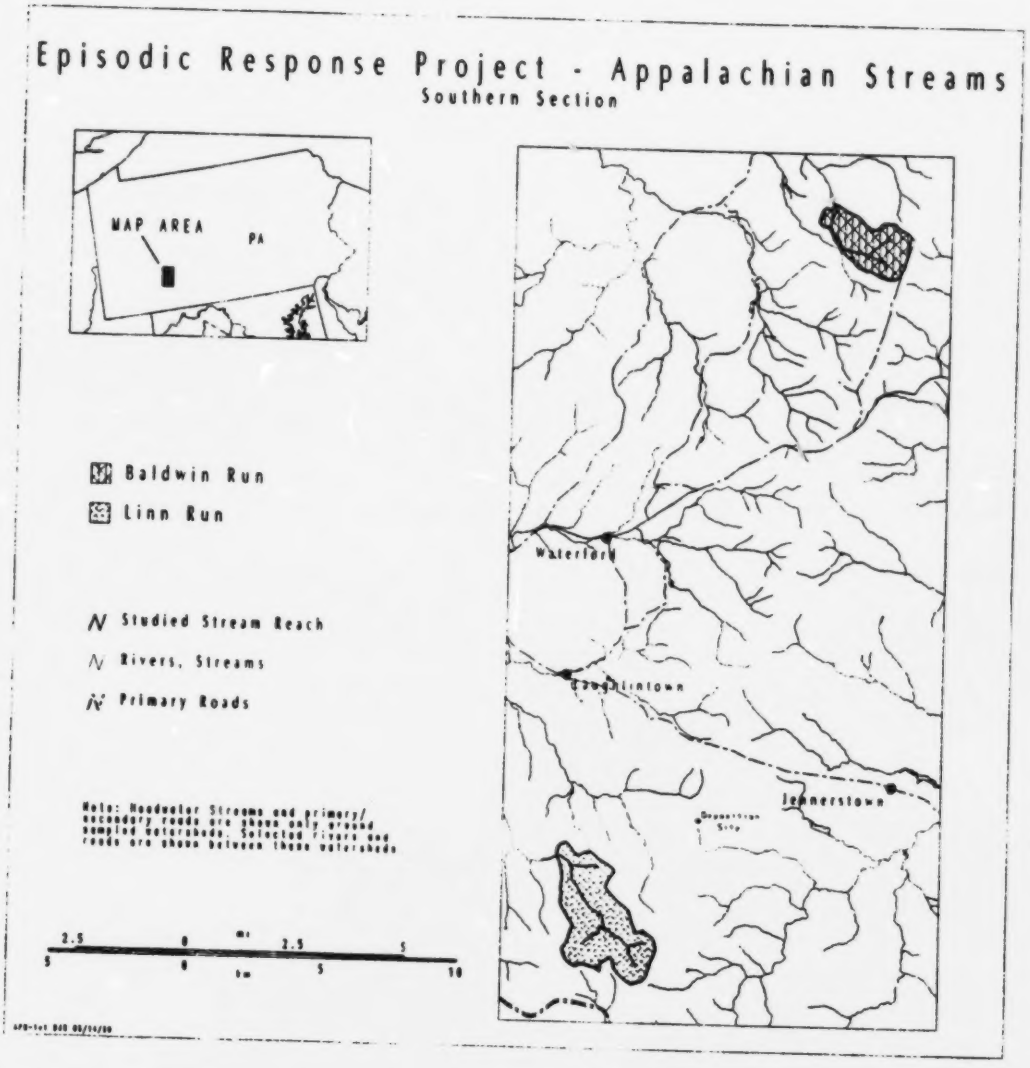

Figure 1. Location map for Linn Run and Baldwin Creek in southwest PA.

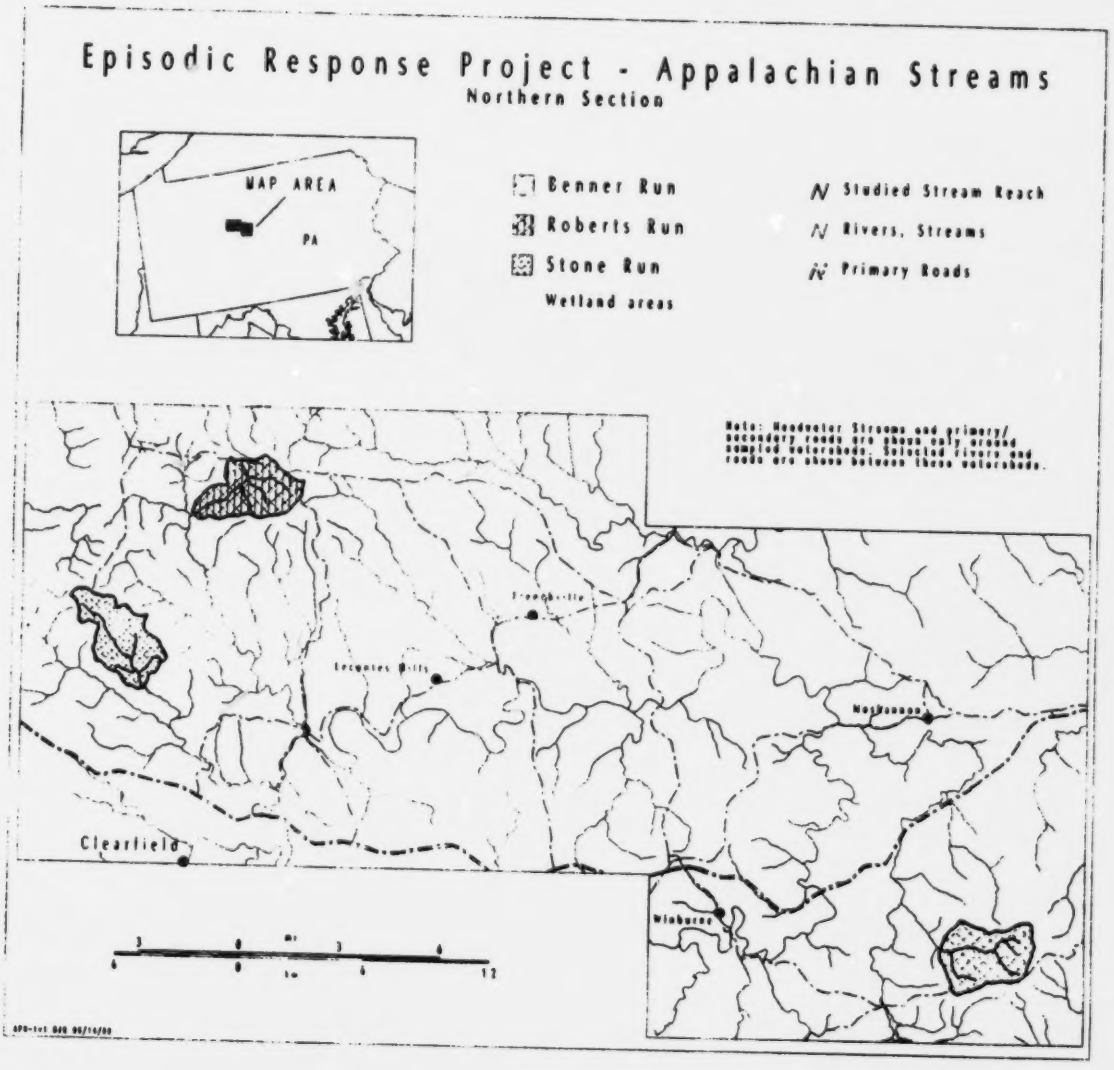

Figure 2. Location map for Benner, Roberts and Stone Runs in northcentral PA.

TABLE 1

Study Site Characteristics

Site	Latitude	Longitude	Basin Area (ha)	Basin Elevation max (m)	Basin Elevation gage (m)	Basin Length (km)	Basin Slope (m/m)	Channel Width (m)	Channel Width/Depth Ratio
Benner Run	40°56'04"N	78°01'22"W	1134	747	582	4.6	0.036	4.9	20.5
Roberts Run	41°10'12"N	78°24'22"W	1070	733	509	5.7	0.039	5.8	31.4
Stone Run	41°05'52"N	78°26'48"W	1156	701	494	5.9	0.035	4.4	16.3
Baldwin Creek	40°21'05"N	79°03'04"W	535	832	439	3.5	0.112	4.7	40.3
Linn Run	40°08'40"N	79°12'37"W	1000	893	573	5.5	0.058	5.0	22.9

moths is occurring on a small upland portion of Roberts Run basin. None of these disturbances appears to be affecting basin hydrology or stream chemistry.

Streams flowing from these basins are second order and large enough to support reproducing populations of fish. Except for Linn Run, channels appear stable with well anchored stones ranging in size from 20 to 60 cm commonly covering the bottom. Areas with sandy deposits and bedrock channel can also be found. Linn Run stream channel is less stable and rocks are of the same size, but not well anchored. Channels are shaded by the forest and rhododendron growing along the banks.

METHODS

The methods employed in the ERP were generally standardized among the three regions: Catskills, Adirondacks, and Northern Appalachians. Methods in the NAP Region will be briefly reviewed in this section to aid interpretation of the preliminary data presented relative to field, lab and QA/QC techniques. A more detailed field training and operations manual (Kilkelly Environmental Associates, 1988) and a quality assurance plan (Peck et al., 1988) developed for this project may be consulted by those requiring more information.

FIELD METHODS-HYDROCHEMISTRY

Stream Discharge

Stream discharge was monitored on each catchment using a Belfort[R] FW-1 water level recorder and stilling well within an instrument shed. Water level was recorded on a weekly strip chart and a Campbell[R] CR-10 data logger. A staff gage was also installed in the channel at each site for reference. Discharge rating curves relating stream stage to discharge were developed by periodically gaging each stream by wading at a reference cross-section using a Marsh-McBirney[R] current meter.

Stilling wells were located in sheds on the stream bank at the mouth of each basin. Sheds were lighted and heated by propane gas, equiped with lightning protection, and fitted with solar panels to recharge the batteries.

Stream Chemistry Sampling

Three methods were employed to sample streams for chemical analysis: ISCO[R] automatic water samplers, grab sampling and USGS Mini-Monitors[R]. ISCO automatic samplers were located in the heated sheds and controlled to sample using a CR-10 data logger program written by Dr. N.J. Peters, USGS, Doraville, GA. Samples were collected on the rising limb, at the peak and falling limb of selected storm hydrographs using this program. ISCO water samples were collected from each site several times per week during storm periods.

All streams were also grab sampled at least bi-weekly at the time of site visits. Samples were collected at mid-depth in the middle of the stream at the shed site.

Mini-Monitors were also used to continuously measure stream pH, temperature, and conductivity. Sites were visited weekly to check and calibrate the pH, temperature, and conductivity probes. Stream pH, temperature and conductivity from the Mini-Monitors were recorded by the CR-10 data logger.

Precipitation and Snowpack Sampling

Precipitation amounts and intensity and snowpack water equivalents were measured on each basin. Snowpacks were also sampled for chemical analysis on each basin. Precipitation was also sampled for chemical analysis at one site near the southwest PA study sites; a similar station was already in operation

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in Centre County, PA which could serve as an index to precipitation chemistry for the three northcentral PA streams.

Precipitation amounts and intensity were measured with tipping-bucket rain gages on the roof of the instrument shed at each site. Data were recorded on the Campbell CR-10 data logger. Air temperature data were also recorded to help interpret the form of precipitation. These gages were not heated and thus did not record snowfall. In addition, gages were influenced by overhead vegetation and thus these data are better considered as throughfall.

Precipitation amounts were also recorded with standard non-recording rain gages equipped with an Alter wind shield on each basin. These gages were located in large openings within fenced enclosures. Anti-freeze was added in winter to prevent freezing and light machine oil in summer to prevent evaporation. Sites were visited weekly and total precipitation was recorded.

Daily precipitation chemistry samples were collected at the Linn Run site in southwest PA using the standard AeroChemetrics[R] wet/dry sampler and a weighing precipitation gage. These samples were collected by personnel of the Loyalhanna Watershed Association (LWA) located in nearby Ligonier, PA under the supervision of Mr. Lysle Sherwin, Executive Director of LWA. Samples were shipped for chemical analysis to Battelle, Pacific Northwest Laboratories in cooperation with Dr. W.R. Barchet. The station operated under protocols similar to those for the MAP3S precipitation chemistry operated by Battelle. This station was assumed to represent precipitation chemistry in southwest PA. A similar MAP3S site for daily precipitation chemistry was already in operation at the Barrens site in Centre County, PA. This site was to be used to represent the three northcentral PA sites.

Snowpack water equivalent and chemistry was also monitored on each catchment on at least a weekly basis if a snowpack was present. A five point snow course for collection of snow samples was established on each catchment near the gaging station in a deciduous forest. One composite snowpack sample from samples taken along the snow course was collected in a standard wet/dry bucket from each basin on each sampling day. Samples were collected at each snow course point with a plexiglass cylinder inserted vertically into the snowpack onto a flat plastic plate inserted between the soil and snow. The number of cores needed at each point was adjusted so that the entire composite sample would provide enough water for chemical analysis. Snowpack water equivalent was computed from the weight of the composite sample, the cylinder diameter, and the number of cores in the composite sample.

Sampling for Stable Isotopes

Sampling of soil water, throughfall and shallow water tables was also conducted for selected events to elucidate basin hydrology using stable isotopes as tracers. Soil water was sampled with three ceramic-cup suction lysimeters on each basin near the gaging station. Throughfall was sampled with three funnel/bottle assemblies on each basin also near the gaging station. On Benner Run one shallow well immediately adjacent to the stream was also sampled. No stable isotope data were included in this report, but reference is made to such sampling.

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FIELD METHODS-BIOLOGY

Electrofishing

Fish populations in the five study streams were estimated using electrofishing and the Zippen (1958) removal procedure. Electrofishing was conducted several times each year in two 100-m long stream sections near the gaging station on each basin. Portable battery-operated (Smith-Root,[R] Vancouver, WA) and gasoline-powered (Coffelt,[R] Denver, CO) electrofishing gear were used. Fish movement into or out of sections was blocked during electrofishing using seines. Electrofishing was also employed to survey fish species diversity at several points within the drainage network on each basin.

Biossays

Bioassay fish were captured by electrofishing and placed in wood frame, screened cages submerged in the stream near the gaging station. Screen was heavy 12 mm mesh Naltex[R] plastic. Inside each cage, 4 L Nalgene[R] jugs with 2 mm mesh fiberglass windows for water circulation were used to hold fish. Each jug contained 6-12 brook trout from the 1988 year class or adult sculpins. A total of 21 or more fish were generally used for each bioassay. Fish were not fed. Bioassays were conducted for 30 d periods in spring and fall in each stream. Fish mortality was observed daily during intensive periods.

Telemetry

During the fall and spring intensive periods, telemetry was used to track movement of 10-15 adult brook trout on Linn Run and Baldwin Creek during episodes. Small one-stage, 2-3 g, 2-3 cm long transmitters operating at 164-166 MHz were inserted into the stomachs of the fish. Transmitters were supplied by L.L. Electronics[R] in Mahomet, IL and Wildlife Materials[R] in Carbondale, IL. Transmitter battery life was advertised at about 30 days. Regurgitation of transmitters and premature battery failure proved to be significant problems. A Telonics TR-2 receiver (Telonics,[R] Mesa, AZ) and a 4 element Yagi antenna were used to track fish. Fish location was marked daily and stream samples collected by hand at each fish location.

Benthic Invertebrate Surveys

Benthic invertebrate samples were collected in each season in the vicinity of the gaging staiton on each stream. A Surber sampler with 30-mesh netting was used to collect five riffle samples at each stream during each visit. Benthos collected was preserved in 70% isopropyl alcohol solution and later identified to family taxonomic level where possible.

LABORATORY METHODS

Water Chemistry Analysis

Water samples were analyzed for pH, conductivity, ANC, DOC, and dissolved silica, ammonium, nitrate, sulfate, chloride, calcium, magnesium, potassium,

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sodium, and total dissolved aluminum concentrations at the Water Laboratory, Environmental Resources Research Institute, Penn State. pH was measured electrometrically using an Orion[R] meter and Ross[R] combination electrode, conductivity was measured using a Yellow Springs[R] conductivity cell, ANC was determined using a Grans plot and a Radiometer[R] automatic titration unit, DOC was determined using infrared detection in a Dohrman Carbon Analyzer,[R] silica, nitrate, and ammonium were determined using automatic colorimetric methods on the Technicon Autoanalyzer,[R] sulfate and chloride were determined using ion chromatography and a Dionex[R] chromatography unit, and the remaining cations were determined using atomic absorption spectroscopy on a Perkin-Elmer[R] spectrophotometer. Samples were filtered with 0.45 micrometer filters except for total dissolved aluminum for which 0.1 micrometer filters were used.

A subset of samples was analyzed for monomeric and organic monomeric dissolved aluminum using procedures basically developed by Driscoll (1984). These samples were analyzed under the supervision of Dr. Brian Dempsey, Dept. Civil Engineering, Penn State. Filter size for these samples was 0.2 micrometers.

Analysis for oxygen-18 stable isotope concentration for selected water samples was conducted by the Earth Science Department, University of Waterloo, Waterloo, Canada.

QUALITY ASSURANCE/QUALITY CONTROL

A detailed quality assurance plan was developed for the project by personnel with Lockheed Engineering and Sciences Company of Las Vegas, NV in cooperation with project researchers. The plan covers the five major data types: stream chemistry, stream hydrology, atmospheric deposition and snowpacks, fish population response, and benthic macroinvertebrates. Data quality objectives (DQO) were established in quantitative terms for precision and bias for each data type. Precision was defined as two times the standard deviation of repeated measurement and total error was computed as precision plus bias. DQO for total error for chemical analysis were generally set at 15%. DQO for detection limits ranged between 0.005 to 0.1 mg/L depending upon the parameter. DQO for tolerable background contamination found in field blank samples ranged from 0.02 to 0.1 mg/L. In addition, representiveness, completeness, and comparability of data were also addressed in at least qualitative terms.

Laboratory quality control was achieved through use of lab blanks, check samples, and analytical split samples. Data quality assessment was obtained through use of field blanks, natural and synthetic audit samples provided by Lockheed, co-located field replicate samples sent to all three participating labs, and LRTAP natural audit samples from Canada. Reports on performance from Lockheed on the natural and synthetic audits were very helpful initially to eliminate bias in measurements. Control charts with warning and control limits were used in the lab for all analytes and in the field for checks on Mini-Monitor pH and conductivity data to detect trends in data quality.

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Audits were also performed of field, laboratory, and data management operations by Lockheed and EPA personnel. Audit reports were used to revise lab and field procedures.

Chemistry data were also verified by using cation/anion balances and comparison of computed and measured conductivity. Samples failing DQO for either of these tests were resubmitted for analysis. If the sample again failed these tests, the observation was flagged appropriately. Only about 2% of all samples analyzed failed either the cation/anion or conductivity test a second time.

Total dissolved aluminum determinations using atomic absorption spectrophotometry and 0.1 micrometer filtration generally gave concentrations less than total monomeric aluminum concentrations determined using the Driscoll (1984) procedure and 0.2 micrometer filtration. The cause of this discrepancy is expected to be the difference in filter pore size and is being investigated.

The results of the water chemistry audit sample analyses conducted through June 1989 are listed in Table 2 for the Northern Appalachian Plateau region. These data were supplied by the Lockheed Environmental Programs Office in January 1991. In this listing Lot designates the type of sample used for the audit; S=synthetic, 9=FN-9 natural, and 10=FN-10 natural samples. The target value for each sample is the expected value and the mean, standard deviation (SD), coefficient of variation (CV) represent laboratory results. Precision is expressed as two times the standard deviation for analytes where the data quality objectives are stated in absolute terms and as two times the CV for analytes where data quality objectives are expressed on a relative or percentage basis. Bias represents the mean difference between target and laboratory values expressed on an absolute or percentage basis. Precision and bias for pH, ANC, conductance, calcium, magnesium, ammonium, nitrate, sulfate, and monomeric aluminum were found to be acceptable. Precision values were above acceptable limits for potassium, sodium, silica, chloride, and total aluminum analysis. Negative bias problems are noted for chloride and DOC. As reports on audit sample analyses were sent to project personnel, these reports were shared with laboratory personnel and steps were taken to try to rectify any problems. Problems with silica and DOC analysis early in the project were discovered in this manner. Overall, results of audit sample analysis appear acceptable with precision of analysis being a greater problem than bias.

A summary of field blank water sample analyses conducted through June 1989 is given in Table 3. Field blanks were created in the field by pouring distilled water into a plastic bottle and submitting the sample blind to the lab for analysis with routine samples collected on that day. Mean and median concentrations often differ indicating the skewed nature of field blank concentrations. Median values indicate that the concentrations in blanks were generally below 0.02 mg/L for cations and below 0.05 mg/L for anions. Conductance of field blanks was approximately that of distilled water in the lab. Later field blanks were made with lower-conductivity distilled and deionized water when available, but the exact date of the shift is not known and supply of this water was often limited. Concentrations of field blanks were judged primarily due to that of the available distilled/deionized water supply.

TABLE 2
Listing of Audit Water Sample Analyses through June 1989

ANALYTE (units)	LOT	Target	n	Mean	SD	CV	Precision	Bias
pH	S	4.45	7	4.48	0.069	--	0.138	0.03
	10	5.15	9	5.21	0.073	--	0.146	0.06
	S	6.53	6	6.40	0.082	--	0.163	-0.14
	9	6.83	9					
	S	7.49	7	7.32	0.103	--	0.206	-0.17
ANC (ueq/L)	S	-39.9	7	-45.6	5.45	-11.9	10.90	-5.7
	10	-0.8	9	-3.5	2.43	-68.9	4.85	-2.7
	S	15.0	6	7.5	8.64	116.0	17.29	-7.6
	S	140.0	7	131.9	13.08	9.9	20%	-6%
	9	152.3	9	150.3	9.68	6.4	13%	-1%
Cond. (µS/cm @ 25 °C)	S	1.4	6	1.9	0.23	12.3	0.46	0.5
	S	17.0	7	16.6	1.00	6.0	2.00	-0.4
	10	23.5	9	22.4	0.67	3.0	1.34	-1.1
	S	45.5	7	45.7	3.26	7.1	14%	< 1%
	9	52.1	9	48.0	0.99	2.1	4%	-8%
Calcium (mg/L)	10	1.82	9	1.66	0.123	7.4	15%	-9%
	S	2.50	6	2.40	0.130	5.4	11%	-4%
	S	4.50	7	4.43	0.169	3.8	8%	-2%
	9	5.02	9	4.80	0.220	4.6	9%	-4%
	S	7.00	7	6.97	0.132	1.9	4%	< -1%
Magnesium (mg/L)	10	0.29	9	0.28	0.014	4.8	0.027	-0.01
	S	0.50	6	0.51	0.019	3.8	8%	3%
	9	0.78	9	0.78	0.064	8.2	16%	0%
	S	0.80	7	0.81	0.021	2.6	6%	< 1%
	S	1.50	6	1.38	0.208	15.1	30%	-8%
Potassium (mg/L)	S	0.25	6	0.25	0.019	7.9	0.039	0.00
	10	0.32	9	0.32	0.060	18.7	37%	< 1%
	S	0.35	6	0.34	0.036	10.6	21%	-2%
	9	0.47	9	0.45	0.033	7.4	15%	-4%
	S	0.60	7	0.59	0.051	8.8	17%	-2%
Sodium (mg/L)	10	0.57	9	0.58	0.068	11.8	23%	2%
	S	0.80	6	0.84	0.075	8.9	18%	6%
	9	2.59	9	2.55	0.156	6.1	12%	-1%
	S	3.50	7	3.56	0.247	6.9	14%	2%
	S	6.00	6	6.15	0.133	2.2	4%	2%
Ammonium (mg/L)	9	0.01	9	0.01	0.011	80.2	0.022	0.00
	10	0.04	9	0.04	0.016	41.0	0.033	0.00
	S	0.10	6	0.10	0.022	21.1	0.044	0.00
	S	0.25	6	0.23	0.027	11.8	24%	-8%
	S	0.50	7	0.48	0.047	9.8	20%	-5%

TABLE 2 (cont)

ANALYTE (units)	LOT	Target	n	Mean	SD	CV	Precision	Bias
Chloride (mg/L)	10	0.30	9	0.33	0.044	13.3	0.088	0.03
	S	0.80	8	0.72	0.115	16.0	32%	-10%
	9	3.96	9	3.75	0.812	21.6	43%	-5%
	S	5.00	7	4.59	0.761	16.6	33%	-8%
	S	15.00	5	15.36	0.460	3.0	6%	-2%
Nitrate (mg/L)	S	0.300	8	0.310	0.0288	9.3	0.0588	0.010
	10	0.886	9	0.913	0.1072	11.7	0.2144	0.027
	9	1.063	9	0.935	0.1154	12.3	0.2308	-0.128
	S	3.000	6	2.950	0.2086	7.1	14%	-2%
	S	6.000	5	6.515	0.9443	14.5	28%	9%
Sulfate (mg/L)	S	2.00	4	1.70	0.078	4.6	0.156	-0.30
	10	5.65	9	5.59	0.462	8.3	17%	-1%
	S	6.00	7	5.56	0.431	7.7	15%	-7%
	9	6.36	9	6.30	0.694	11.0	22%	-1%
	S	10.00	8	9.88	0.266	2.7	6%	-1%
Silica (mg/L)	S	0.70	4	0.69	0.075	10.9	0.150	-0.01
	S	3.00	9	2.86	0.213	7.5	15%	-5%
	10	3.47	9	3.37	0.349	10.4	21%	-3%
	9	4.07	9	4.01	0.288	7.2	14%	-1%
	S	7.00	6	6.64	0.329	5.0	10%	-5%
DOC (mg/L)	S	2.5	6	3.0	0.36	12.1	24%	-20%
	10	3.3	9	3.5	0.33	9.4	19%	6%
	9	4.4	9	4.3	0.65	15.1	30%	-3%
	S	5.0	6	5.5	0.34	6.2	12%	-10%
	S	10.0	6	10.6	0.16	1.5	3%	6%
Al, total (ug/L)	9	41	9	64	46.4	72.6	92.8	23
	S	50	7	53	4.3	8.2	8.6	3
	10	187	9	170	26.7	15.7	53.4	-17
	S	400	7	428	17.3	4.0	8%	+7%
	S	750	6	825	27	3.3	7%	+10%
Al, mono. (ug/L)	9	13	8	12	5.2	43.1	10.4	-1
	S	50	4	48	3.9	8.2	7.8	-2
	10	158	8	164	4.6	2.8	9.2	6
	S	400	4	383	10.4	2.7	5%	-4%
	S	750	3	722	5.5	0.8	2%	-4%
Al, org. mono. (ug/L)	9	7	8	8	1	12.2	2	1
	10	42	8	39	6	15.5	12	-3

TABLE 3

Summary of Field Blank Water Sample Analysis through June 1989

Analyte	n	Mean	SD	Median
pH	33	5.43	0.182	5.39
ANC (μeq/L)	34	-0.87	4.29	-0.95
Cond. (μS/cm @ 25 °C)	33	2.56	0.785	2.55
Calcium (mg/L)	34	0.031	0.034	0.020
Magnesium (mg/L)	34	0.0076	0.0065	0.0065
Potassium (mg/L)	34	0.0187	0.0156	0.015
Sodium (mg/L)	34	0.0199	0.0171	0.0155
Ammonium (mg/L)	34	0.0182	0.0210	0.0150
Chloride (mg/L)	34	0.0705	0.0907	0.0435
Nitrate (mg/L)	34	0.137	0.276	0.055
Sulfate (mg/L)	34	0.0339	0.0677	0.000
Silica (mg/L)	34	0.0779	0.0630	0.050
DOC (mg/L)	34	1.19	1.01	1 09
Al, Total (μg/L)	34	15.6	41.2	5.5
Al, mono. (μg/L)	7	7.3	0.60	8.0
Al, org. mono.(μg/L)	5	0.4	0.89	0.00

RESULTS

DEPOSITION

Precipitation amounts occurring on the five study areas during the first year are summarized in Figure 3 using data from shielded non-recording gages. Total precipitation for the period November 1988 through June 1989 ranged from about 600 to 950 mm on the basins. Normal precipitation in Pennsylvania is about 40 inches or 1016 mm annually. Precipitation received on these basins indicates an above-normal year. On Linn Run, data were only available from early March through June 1989, but precipitation totals at this site nearly equalled that on Baldwin Creek over the longer period. It appears that the Linn Run basin received more precipitation than the other basins, perhaps due to its higher elevation. The winter of 1988-89 produced few significant snowfall events, with no snowpack lasting more than one week and no major snowmelt events on these basins.

Data from the deposition monitoring site near the Linn Run basin was used to index daily precipitation amounts, wet deposition chemical concentrations and daily wet deposition chemical loadings. Data cover the period February through June 1989. Concentrations of chemical constituents in wet deposition are shown in Figures 4-6, precipitation amounts in Figure 7 and chemical loadings in Figures 8 and 9.

HYDROLOGY

The general hydrologic response of the five watersheds is best portrayed by the streamflow hydrographs for the period October 1988 - June 1989 (Figures 10-14). Figure 10 shows a very flashy response on Linn Run with nearly 20 major events during the period of record compared to only about six on nearby Baldwin Creek (Figure 11). Part of this difference may be due to greater precipitation intensity and/or amounts on Linn Run basin as previously described. Watershed characteristics may also play a role in explaining differences. Responses of Benner, Roberts and Stone Runs (Figures 12-14, respectively) were quite similar with about six major events on each basin, but Benner Run does appear to be somewhat less responsive to rainfall. Again, despite the close proximity of these latter three basins, differences in storm rainfall causing event differences cannot be ruled out.

Flow duration curves for the five streams for October 1988 through May 1989 can be used to compare flow regimes on a common basis. Flow duration curves for the three northcentral Pennsylvania streams are quite similar (Figure 15). The Benner Run curve shows an almost total lack of flow rates greater than 0.1 $m^3 s^{-1} km^{-2}$. Much higher flows are found on Baldwin Creek and Linn Run (Figure 16) than on the three northcentral streams. Baldwin Creek appears to reach peaks less often than Linn Run, but for major events Baldwin reaches higher peaks and maintains that flow longer. Overall, differences among flow duration curves are quite subtle and more data are needed for a meaningful flow duration analysis.

All five watersheds have been instrumented with equipment needed to collect samples for hydrograph separation using natural isotopes. Three throughfall collectors have been placed on each watershed to sample the precipitation or "new" water component. Three suction lysimeters were also

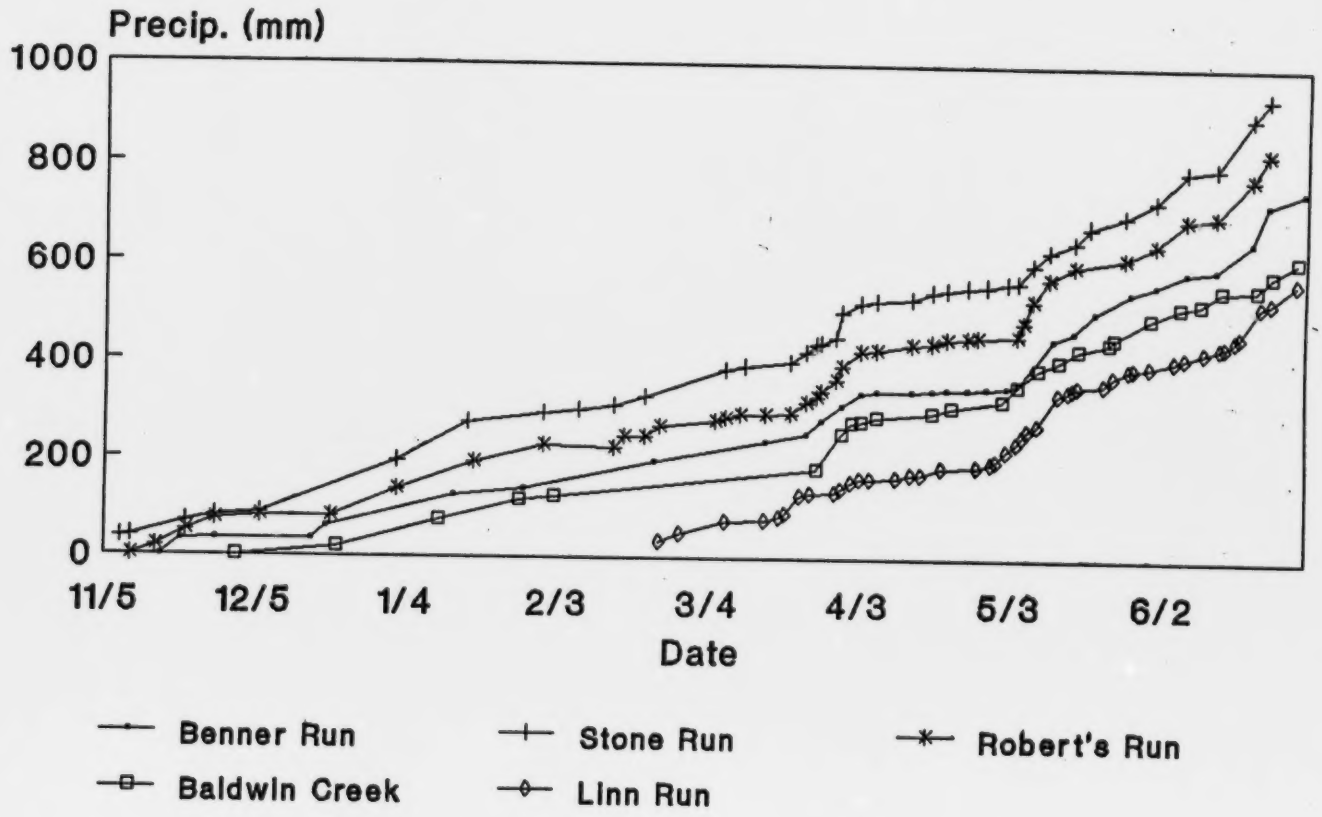


Figure 3. Accumulated precipitation on the five study basins.

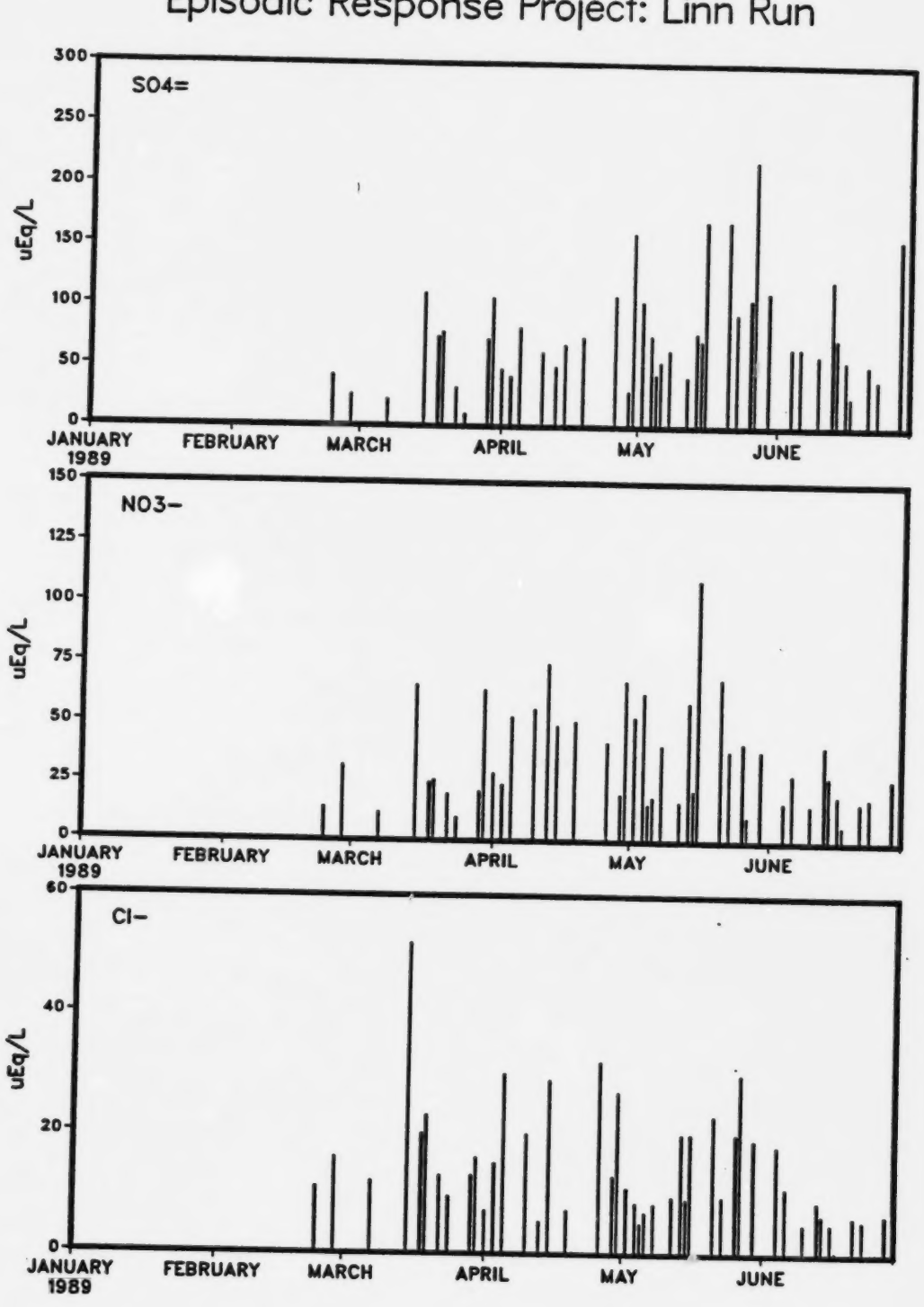


Figure 4. Anion concentrations in daily wet deposition samples at the Linn Run site.

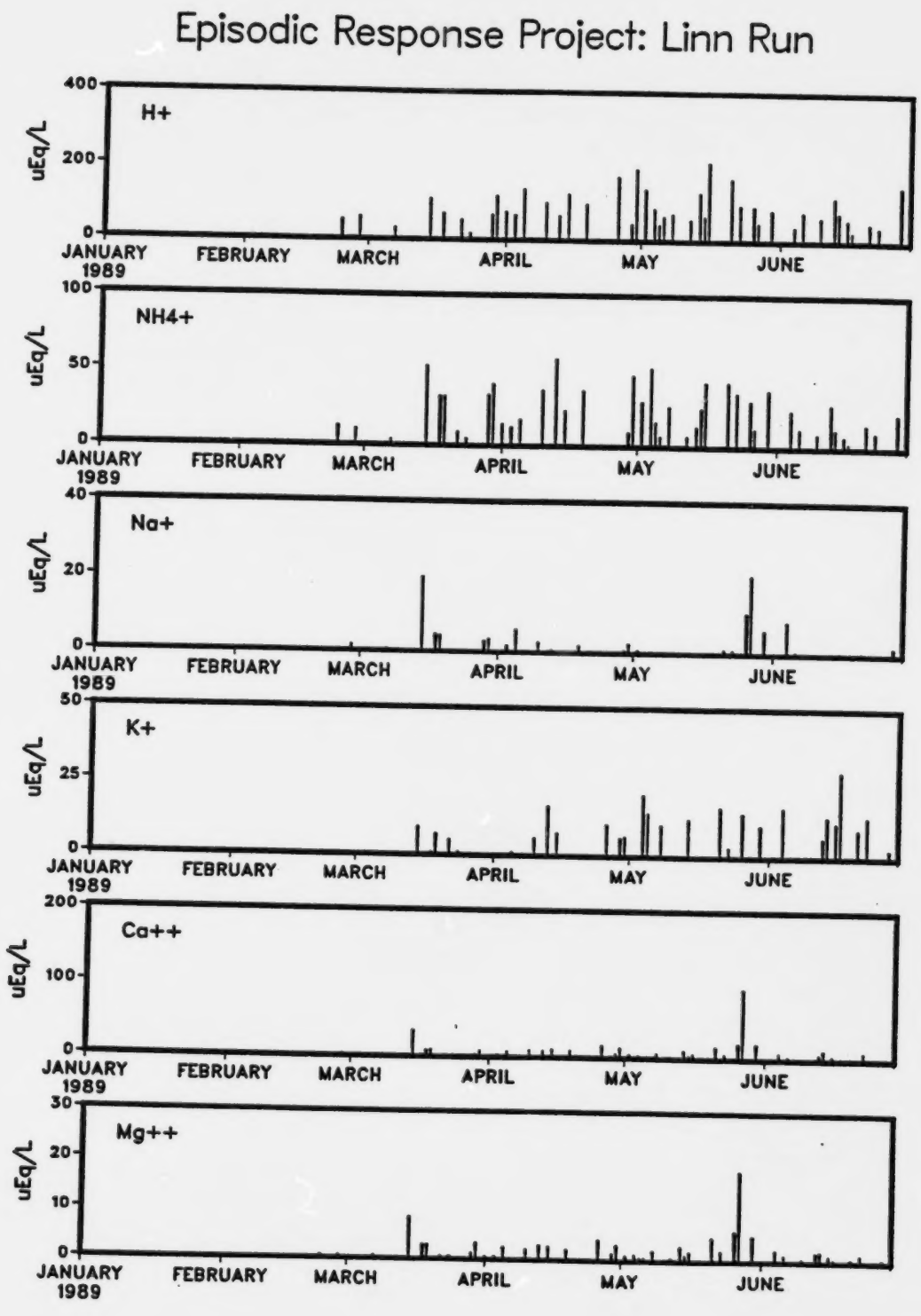


Figure 5. Cation concentrations in daily wet deposition samples at the Linn Run site.

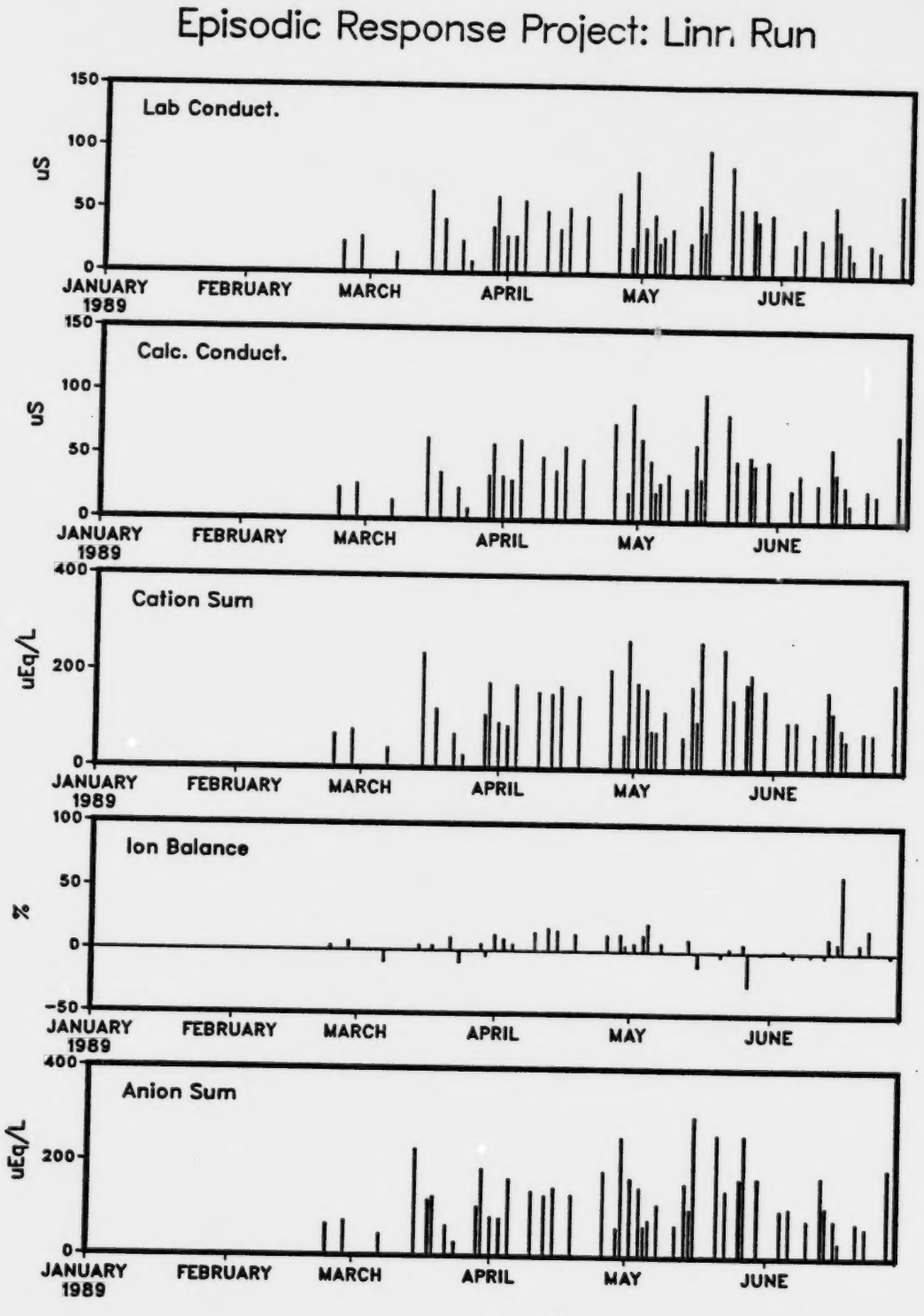


Figure 6. Conductivity and cation/anion balances in daily wet deposition samples at the Linn Run site.

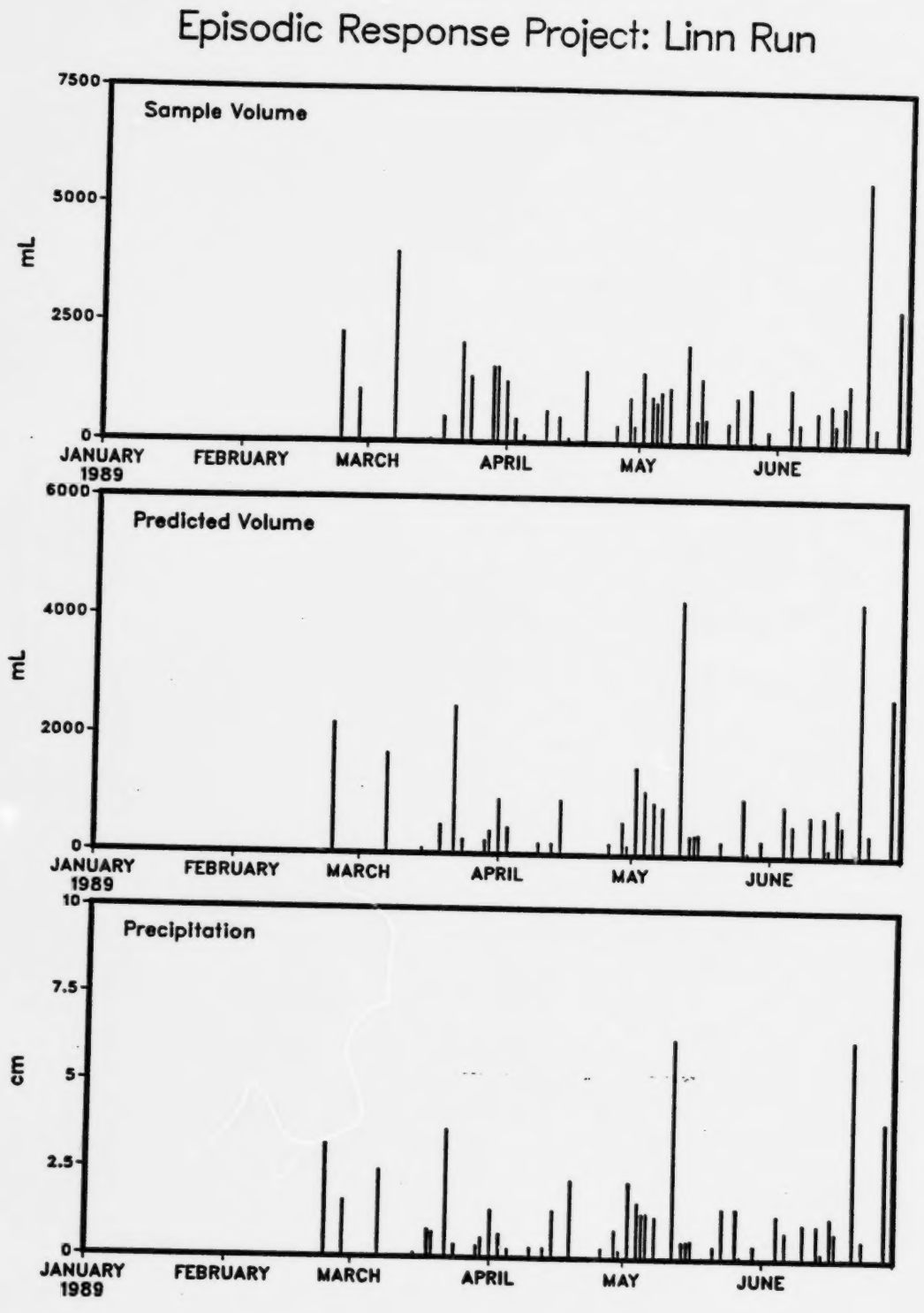


Figure 7. Daily precipitation amounts and daily wet deposition sample volumes at the Linn Run site.

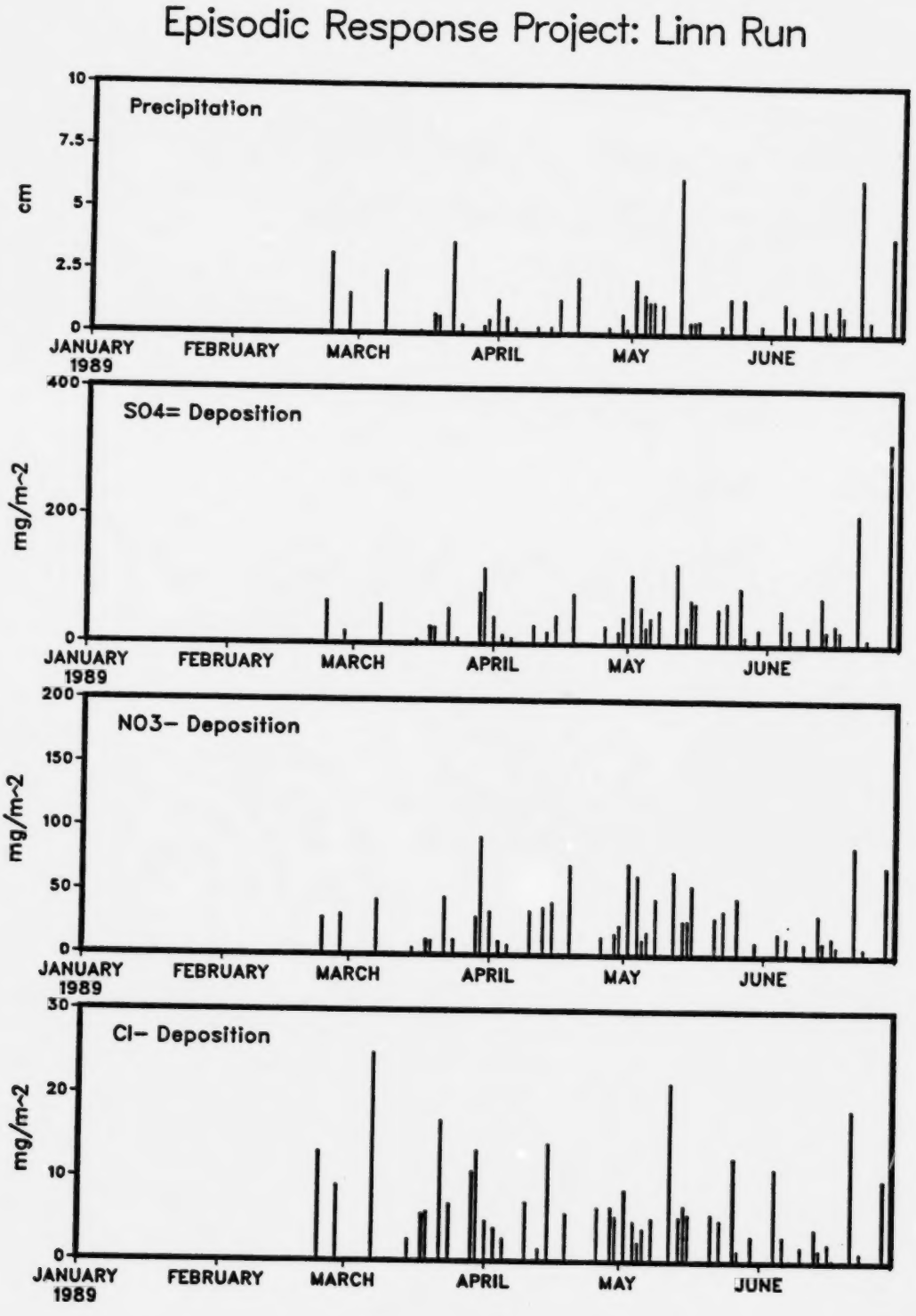


Figure 8. Daily loads of anions in wet deposition at the Linn Run site.

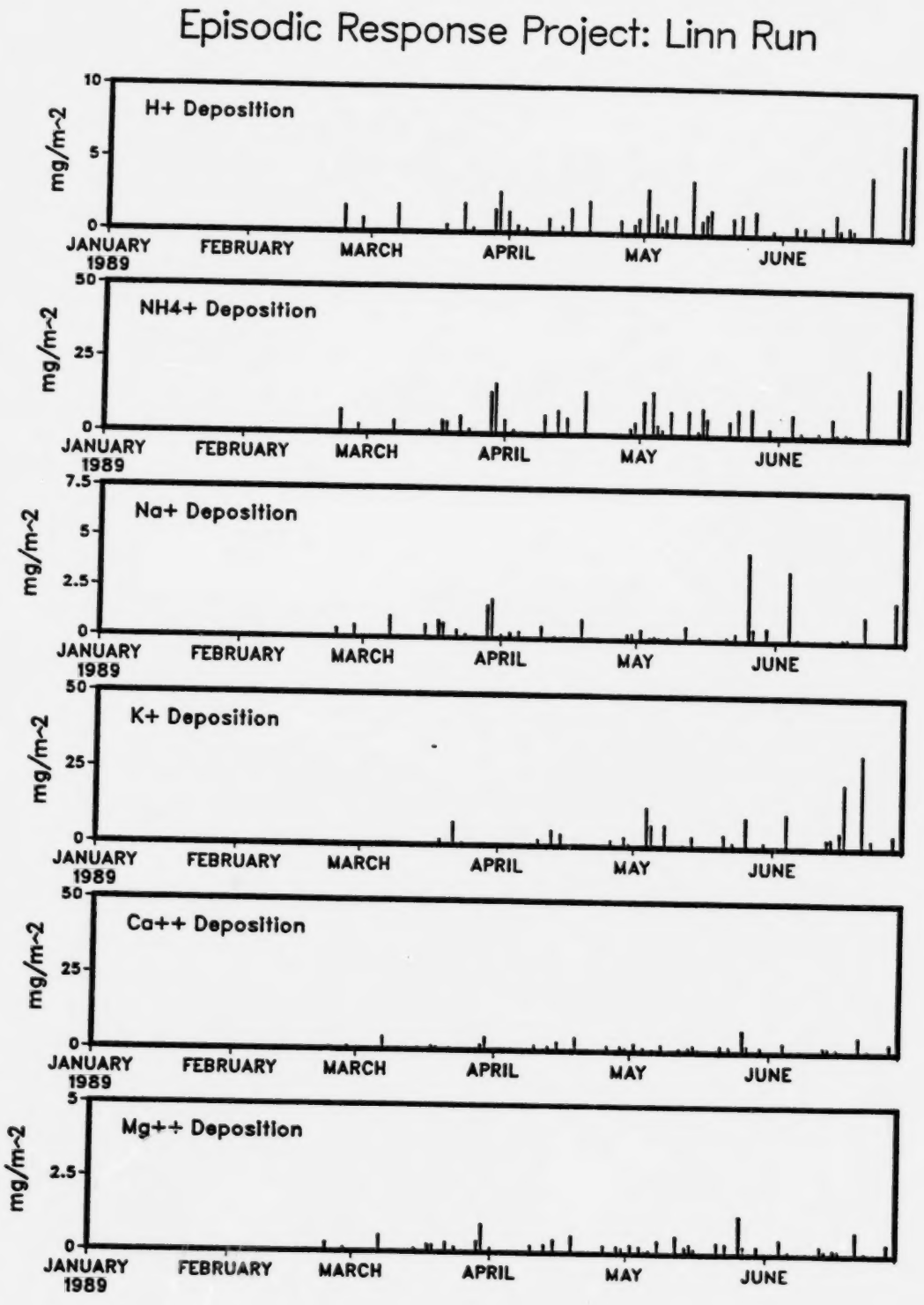


Figure 9. Daily loads of cations in wet deposition at the Linn Run site.

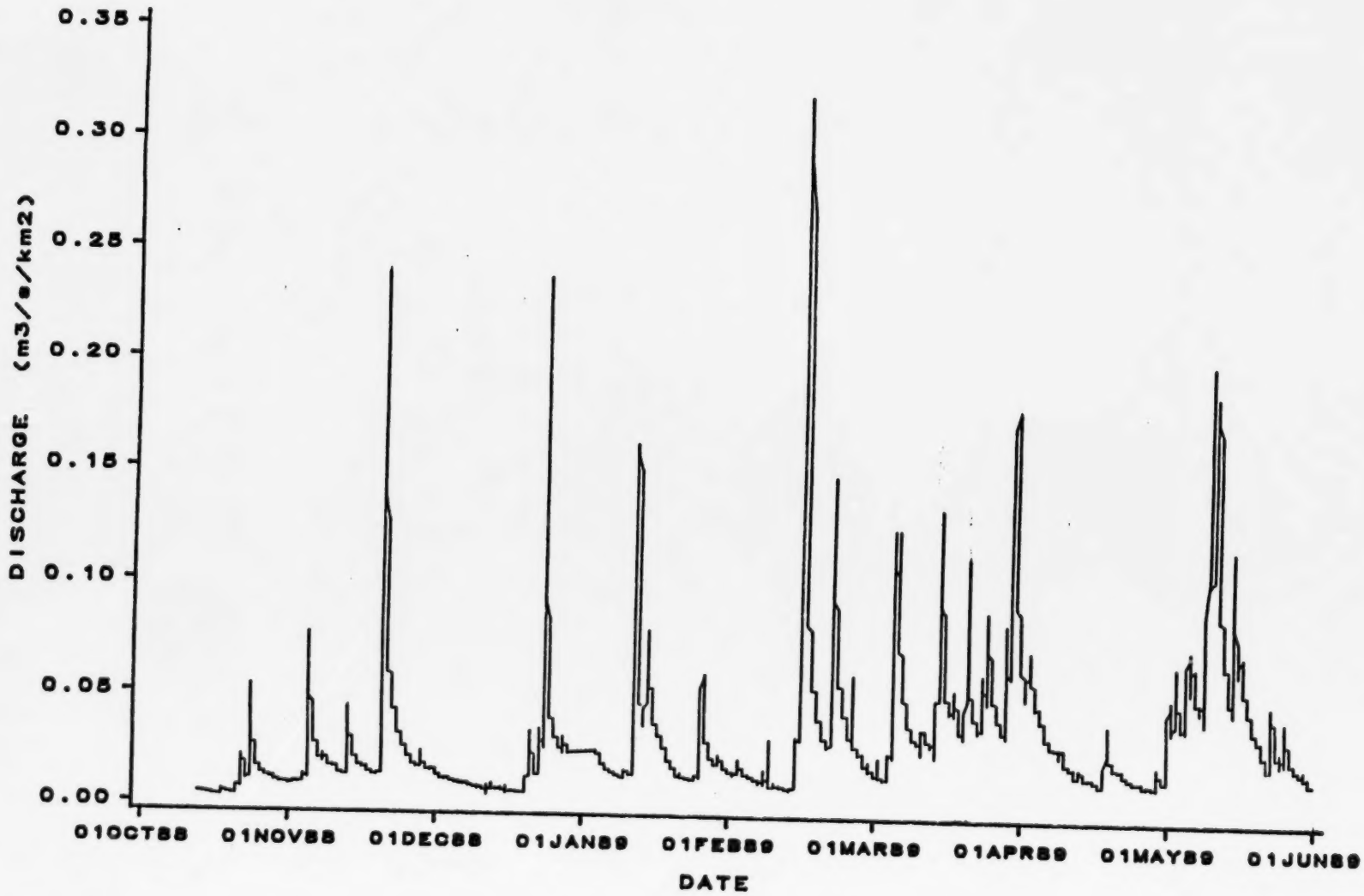


Figure 10. Streamflow hydrograph for Linn Run.

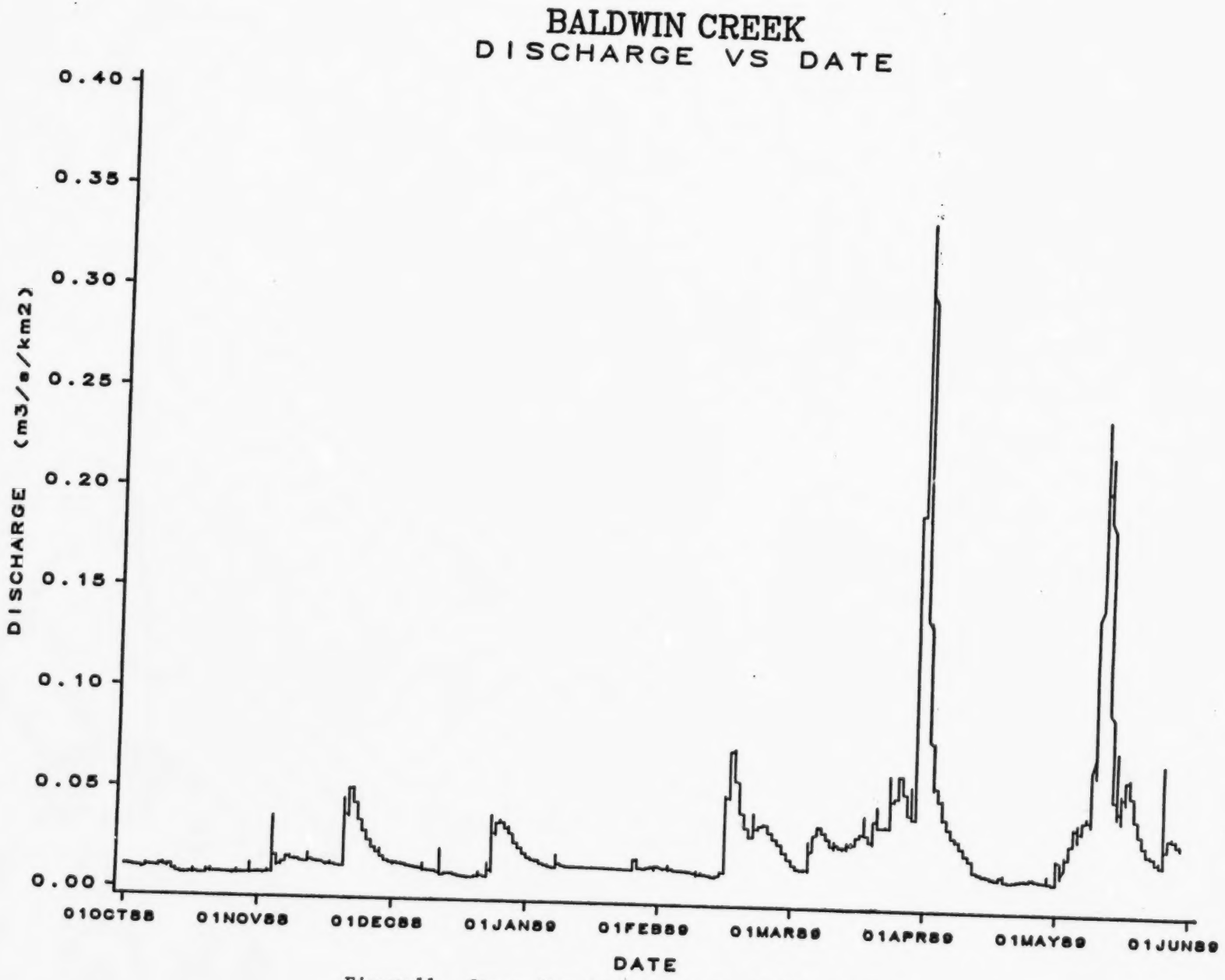


Figure 11. Streamflow hydrograph for Baldwin Creek.

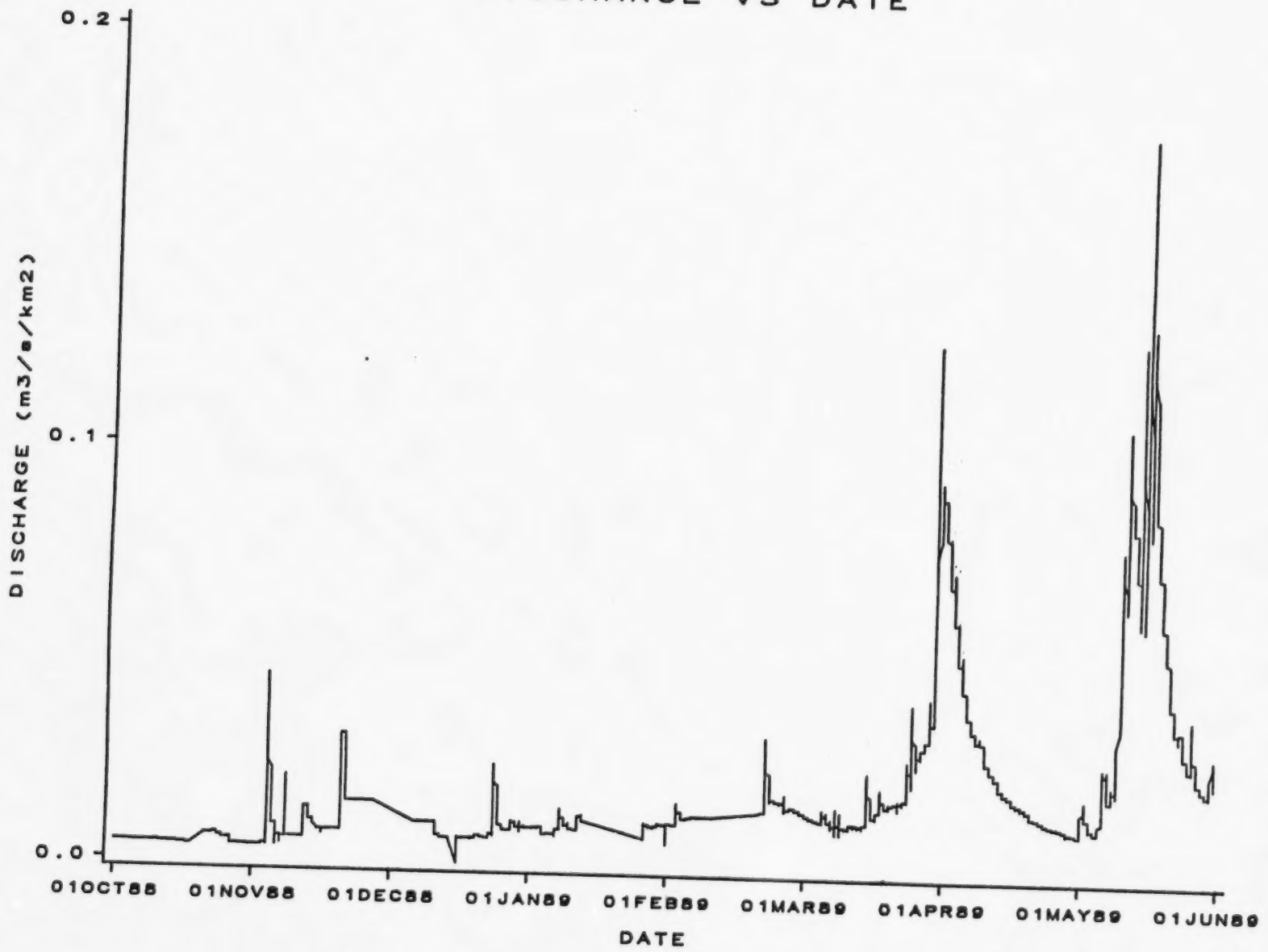


Figure 12. Streamflow hydrograph for Benner Run.

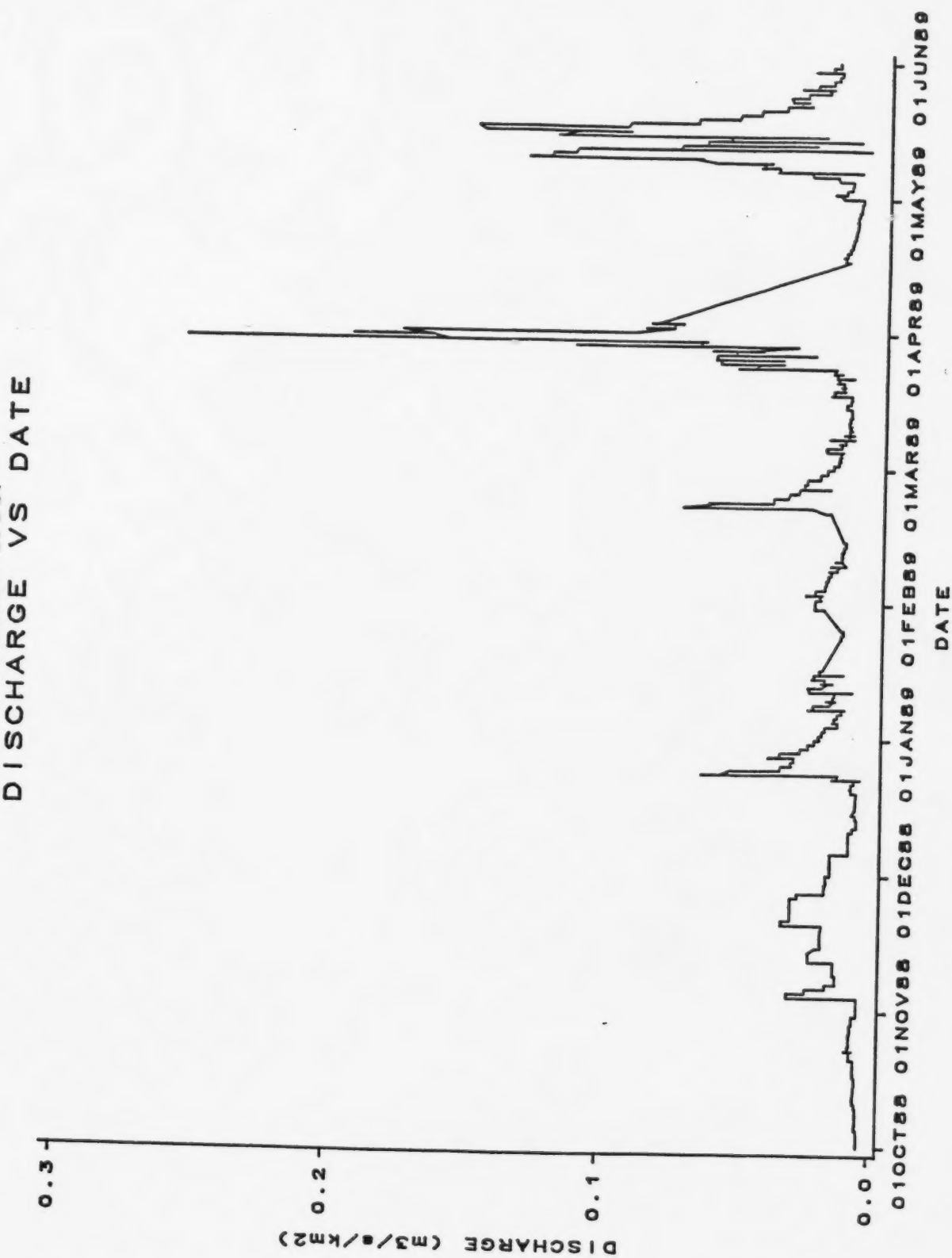


Figure 13. Streamflow hydrograph for Roberts Run.

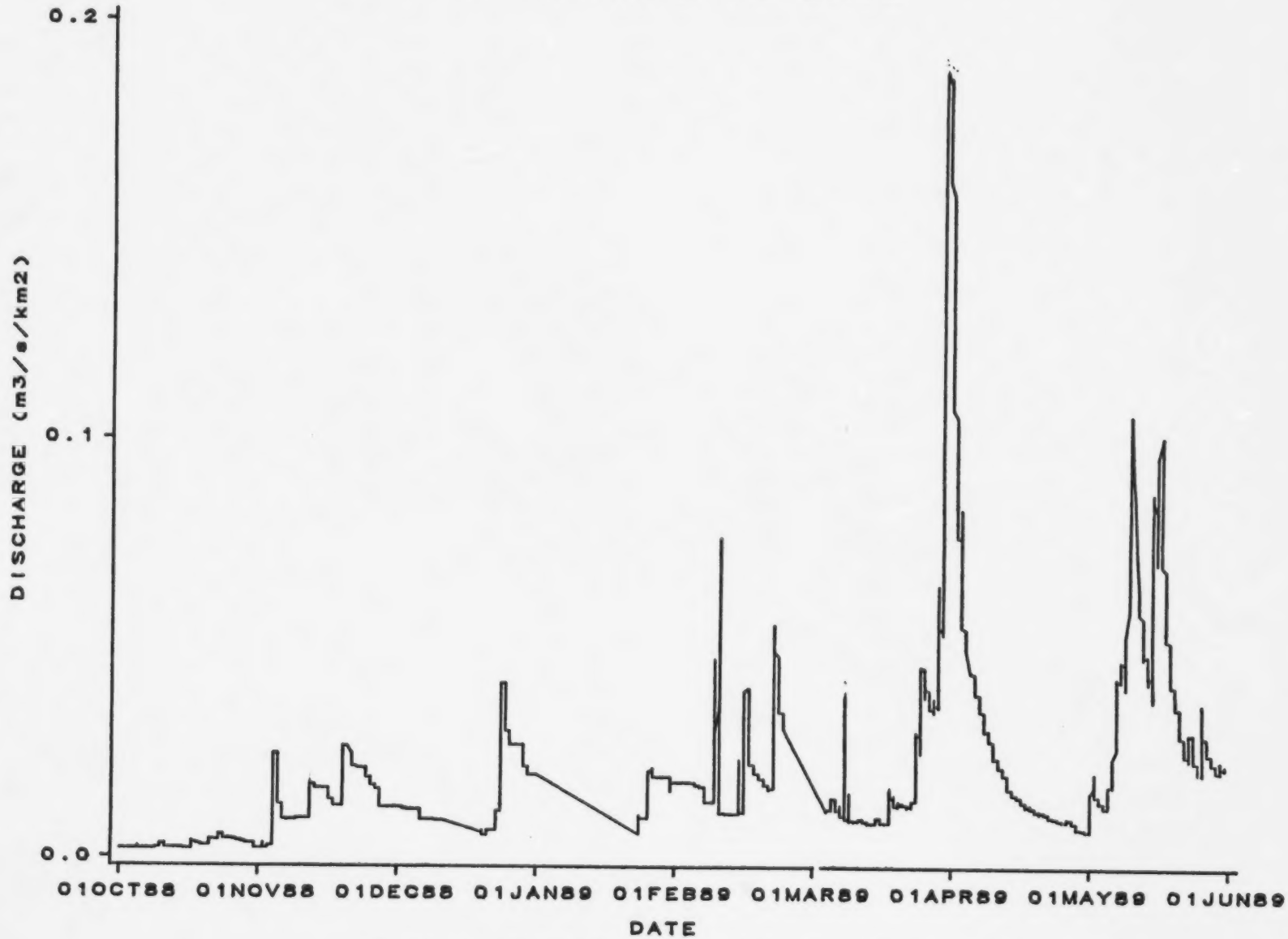
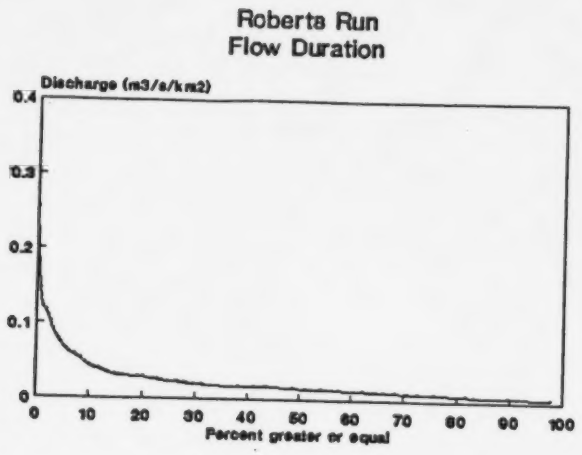
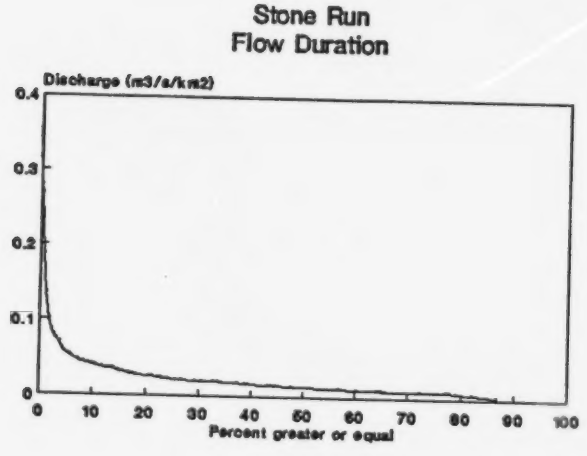


Figure 14. Streamflow hydrograph for Stone Run.





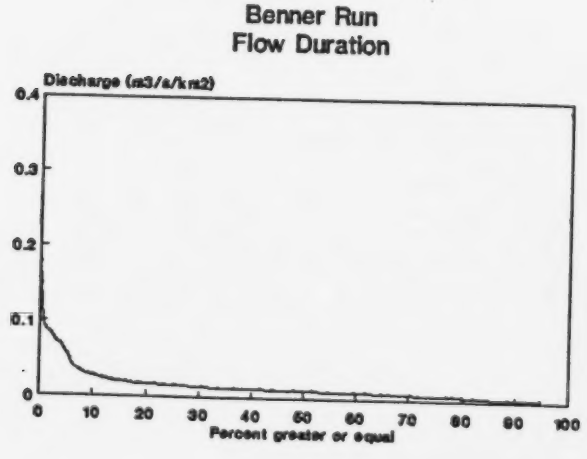


Figure 15. Flow duration curves for northcentral Pennsylvania streams for October 1988 to June 1989.

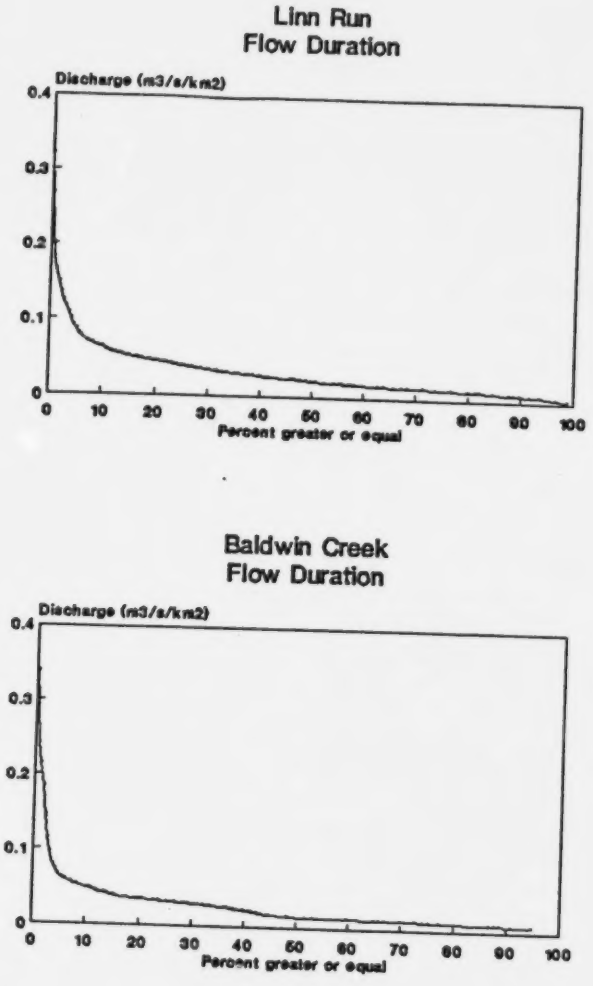


Figure 16. Flow duration curves for two southwest Pennsylvania streams for October 1988 to June 1989.

installed on each watershed in the near-stream, unsaturated zone to sample soil water. Baseflow samples which serve as the "old" water component have been collected by grab sampling. Stormflow samples have been collected using the automated ISCO samplers. Two shallow wells have also been installed for the purpose of comparing shallow groundwater with baseflow samples. No problems with equipment have been encountered with the exception of one broken lysimeter which was replaced.

Sampling for stable isotopes began in early March 1989. Six concurrent events were intensively sampled on all five streams. An average of fifteen stormflow samples were collected on each hydrograph to characterize the episodes isotopically. All samples are presently being stored in sealed, leak-proof bottles. Those samples chosen for analysis will be sent to the Isotope Laboratory in Waterloo, Canada. Due to the high cost of sample analysis, diagnostic samples for selected events were sent to determine if the differences in oxygen-18 concentration were large enough to permit separation. If differences are present, the remaining samples for each event will be analyzed. A natural lake water audit sample (FN-10) is sent with each batch of samples. A two-month laboratory back-log and the diagnostic samples approach has delayed the separation of stormflow hydrographs.

STREAM CHEMISTRY

A summary of all stream chemistry data for stormflow and baseflow from October 1988 to June 1989, for each stream is given in Table 3. Medians rather than means are given in Table 4, since nearly all distributions were non-normal. Also, the number of samples for total monomeric and organic monomeric Al is much lower than that for other analyses making direct comparisons with total Al invalid. Calcium is the dominant cation and sulfate the dominant anion in all streams. Conductivities (25-35 $\mu S/cm$) are quite low as is typical of undisturbed, sandstone/shale bedrock catchments in this region. ANC and pH data indicate that Benner Run has the best buffered water of the three streams in northcentral Pennsylvania. Baldwin Creek is much less acidic than Linn Run in the southwest PA group. Other noteworthy features are: the rather high NO_3 concentration of southwest PA streams compared to northcentral streams, the higher DOC concentration in Roberts Run which is probably related to the presence of small bogs on the upper slopes of this catchment, and the large differences in total dissolved Al among basins.

The annual patterns of pH, total dissolved Al and ANC in relation to flow are quite revealing. pH and ANC are both negatively (significance $\alpha = 0.0001$) correlated with flow on all streams. As can be seen in Figures 17-21 for pH and Figures 22-26 for ANC, flow increases throughout the year are accompanied by declines in pH and ANC. In contrast, total dissolved Al concentrations are positively correlated ($\alpha = 0.0001$) with flow on all streams. Flow increases are accompanied by increased total dissolved Al content (Figures 27-31) on all streams.

The nature of episodic chemistry in these streams can be further documented by looking at data for two rainfall periods: March 24 to April 5, 1989 and May 5-15, 1989. For the March 24 - April 5 period, the expected pH and ANC declines and increases in total dissolved Al with increasing flow can be seen on all streams (Figures 32-41). DOC generally increases erratically with flow increases on all streams; but NO_3, SO_4, Cl, and sum of base cations

TABLE 4

Median Stream Chemistry for October 1988 to June 1989

PARAMETER	MEDIAN CONCENTRATIONS				
	BENNER	ROBERTS	STONE	LINN[1]	BALDWIN
pH (neg log $[H^+]$moles/L)	5.8	5.0	5.2	5.4	6.2
Ca (µeq/L)	80	96	100	162	167
Mg (µeq/L)	51	75	65	58	90
K (µeq/L)	19	18	14	11	21
Na (µeq/L)	35	19	22	20	21
NH_4 (µeq/L)	1	1	1	1	1
SO_4 (µeq/L)	106	187	192	221	202
NO_3 (µeq/L)	38	30	8	89	81
Cl (µeq/L)	48	24	28	28	37
DOC (mg/L)	2.5	2.9	2.3	2.0	1.9
ANC (µeq/L)	7.6	-7.9	-5.2	1.4	16.8
Al-total dissolved µg/L	50	118	197	156	32
-total monomeric[2] (µg/L)	76	206	316	330	48
-org. monomeric[2] (µg/L)	42	32	30	26	24
SiO_2 (mg/L)	4.0	3.4	3.95	3.5	4.2
conductivity (µS/cm)	24.4	32.0	31.3	34.3	35.3

1 Linn Run includes data only up to 4/7/89.
2 Number of samples for total monomeric and organic monomeric Al lower than for total dissolved Al data.

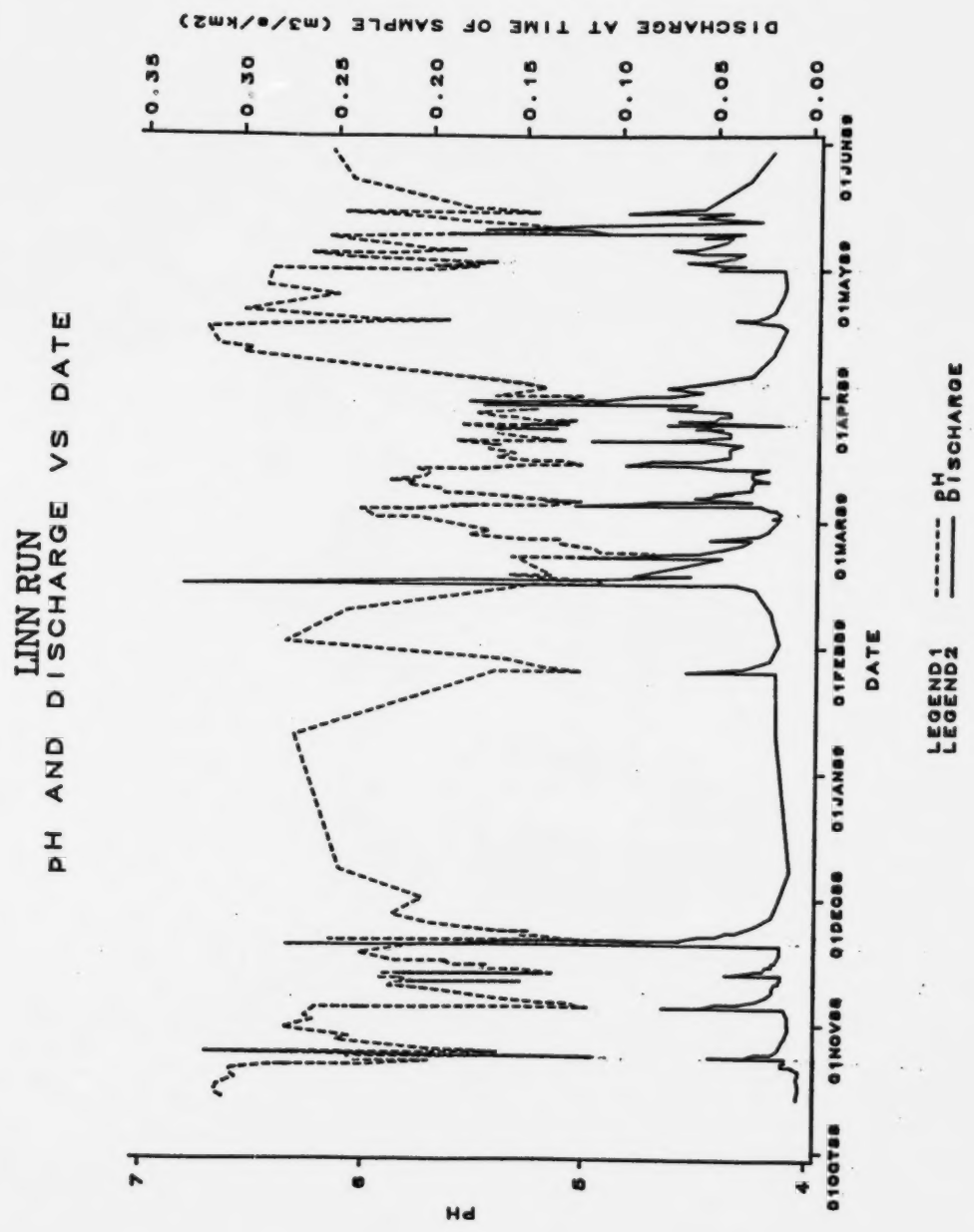


Figure 17. pH and discharge variations for Linn Run for October 1988 to June 1989.

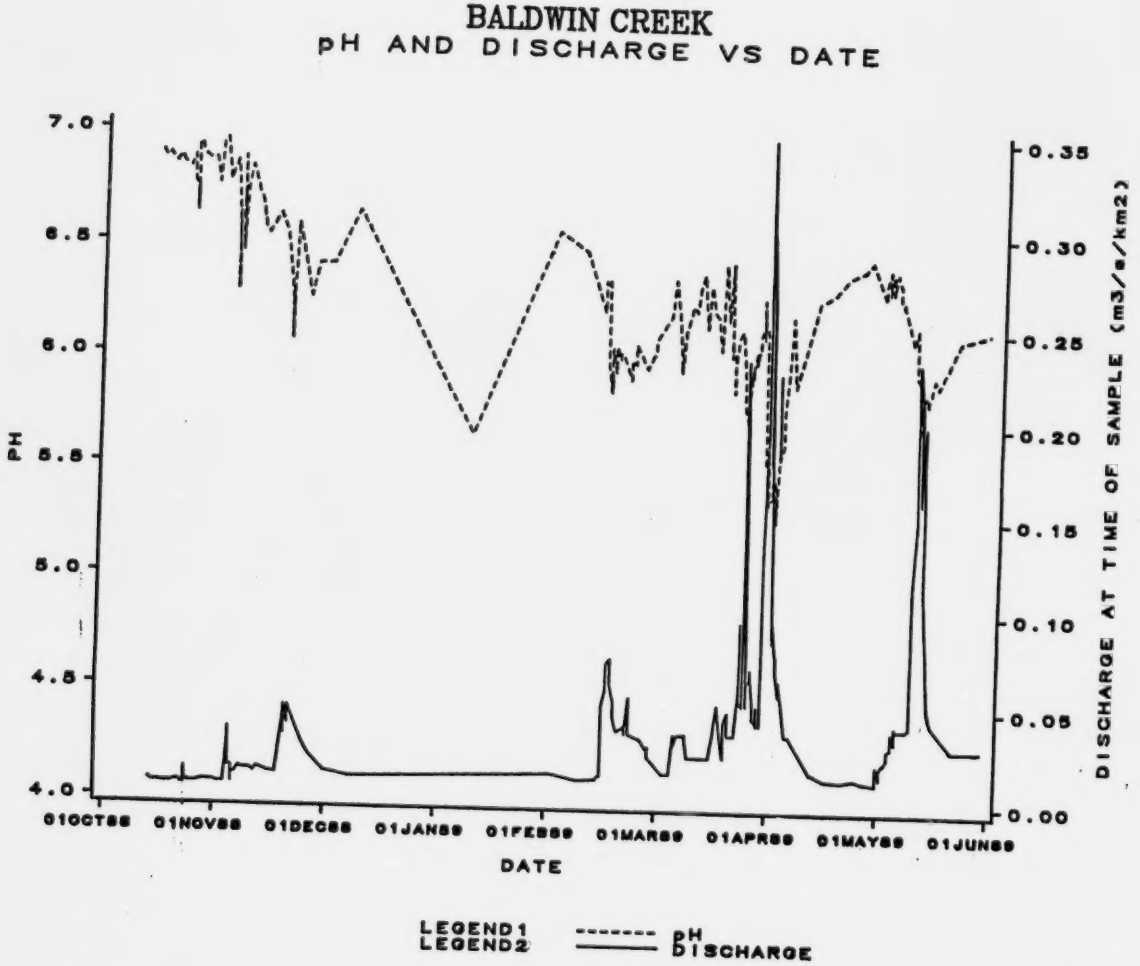


Figure 18. pH and discharge variations for Baldwin Creek for October 1988 to June 1989.

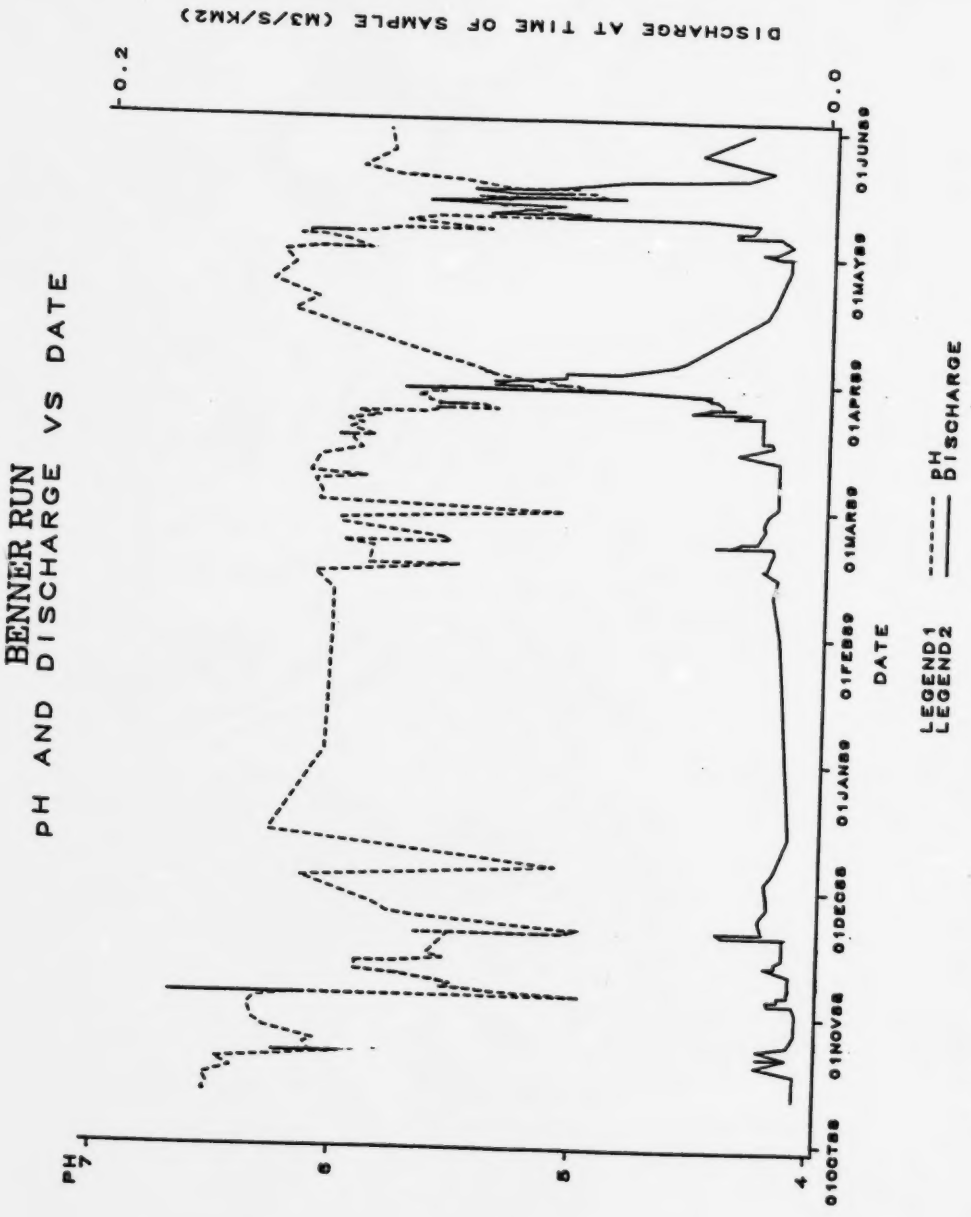


Figure 19. pH and discharge variations for Benner Run for October 1988 to June 1989.

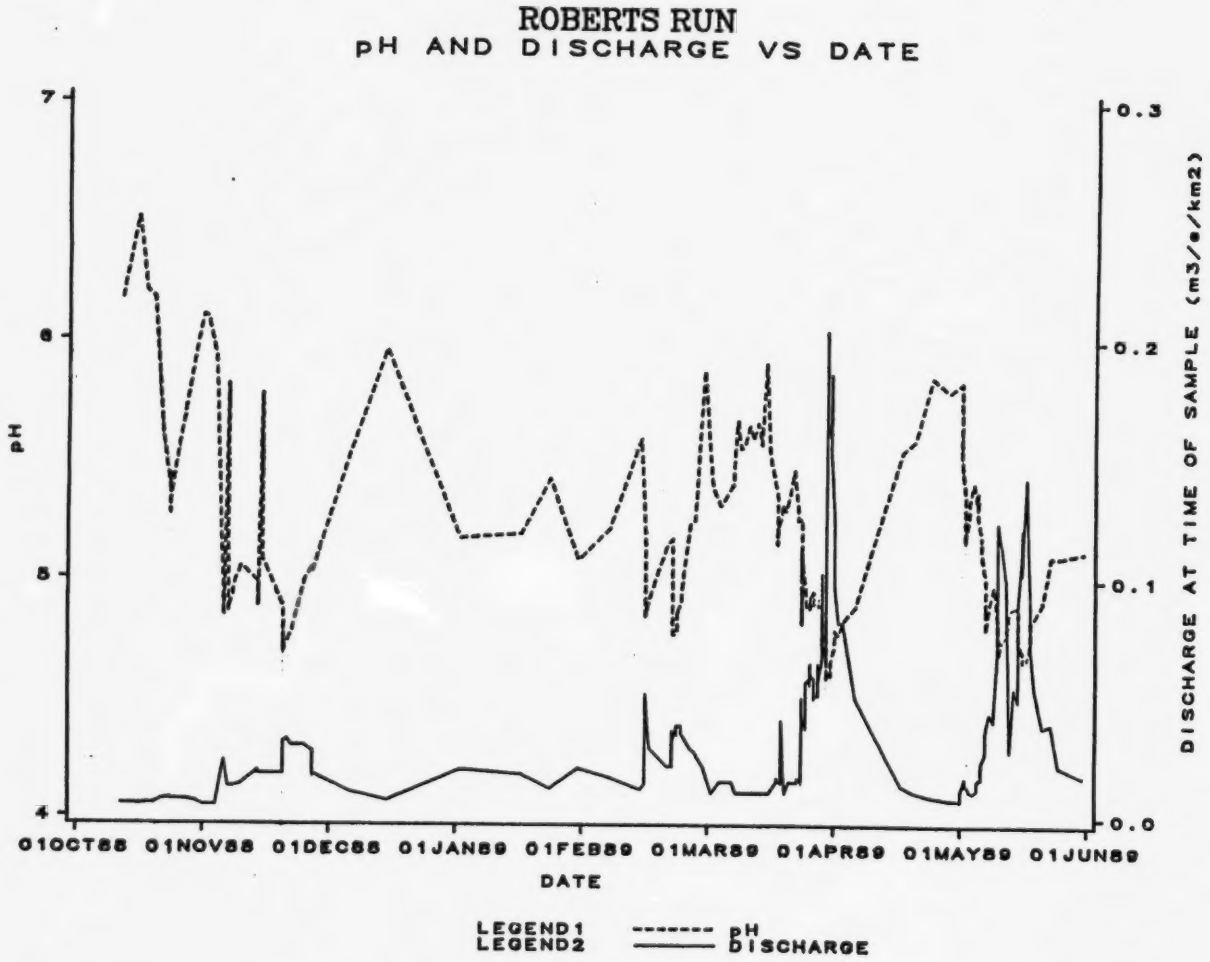


Figure 20. pH and discharge variations for Roberts Run for October 1988 to June 1989.

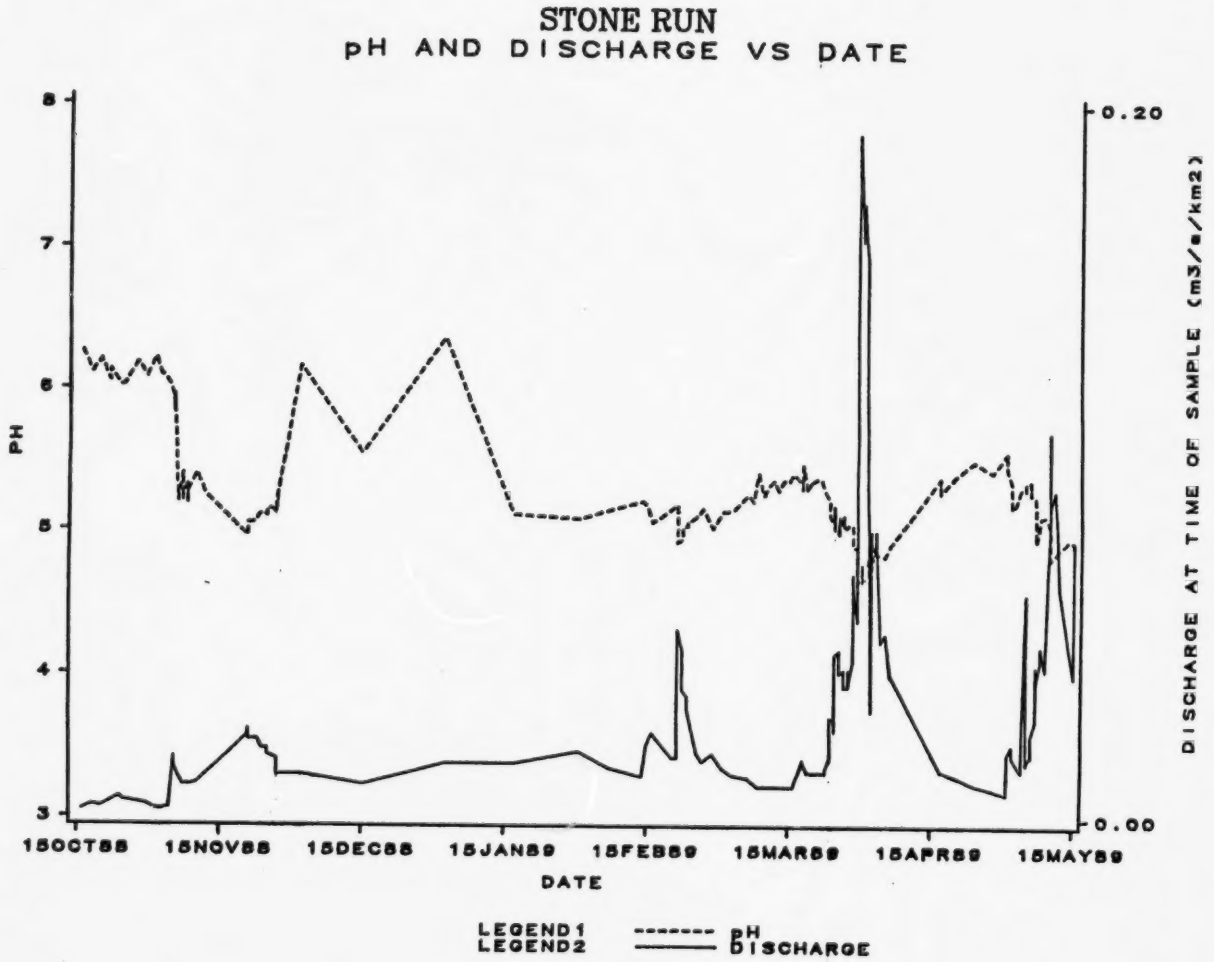


Figure 21. pH and discharge variations for Stone Run for October 1988 to June 1989.

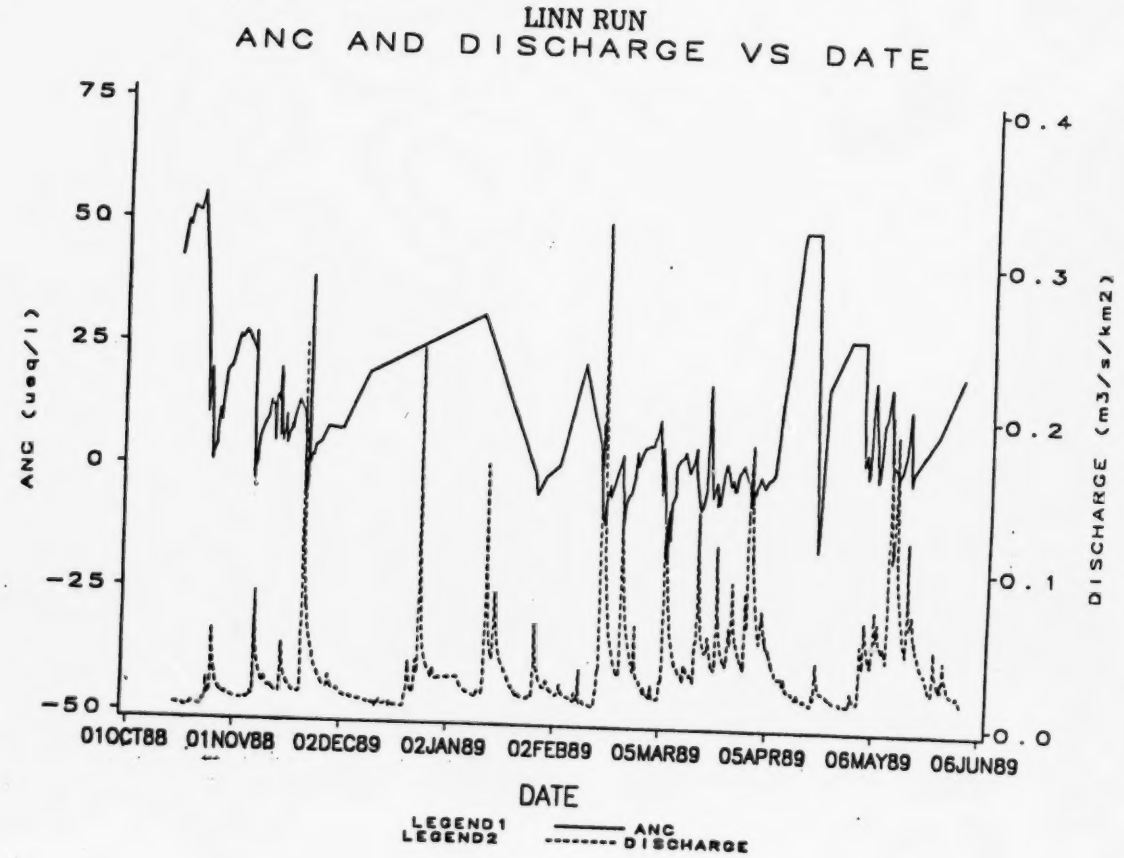


Figure 22. ANC and discharge variations for Linn Run for October 1988 to June 1989.

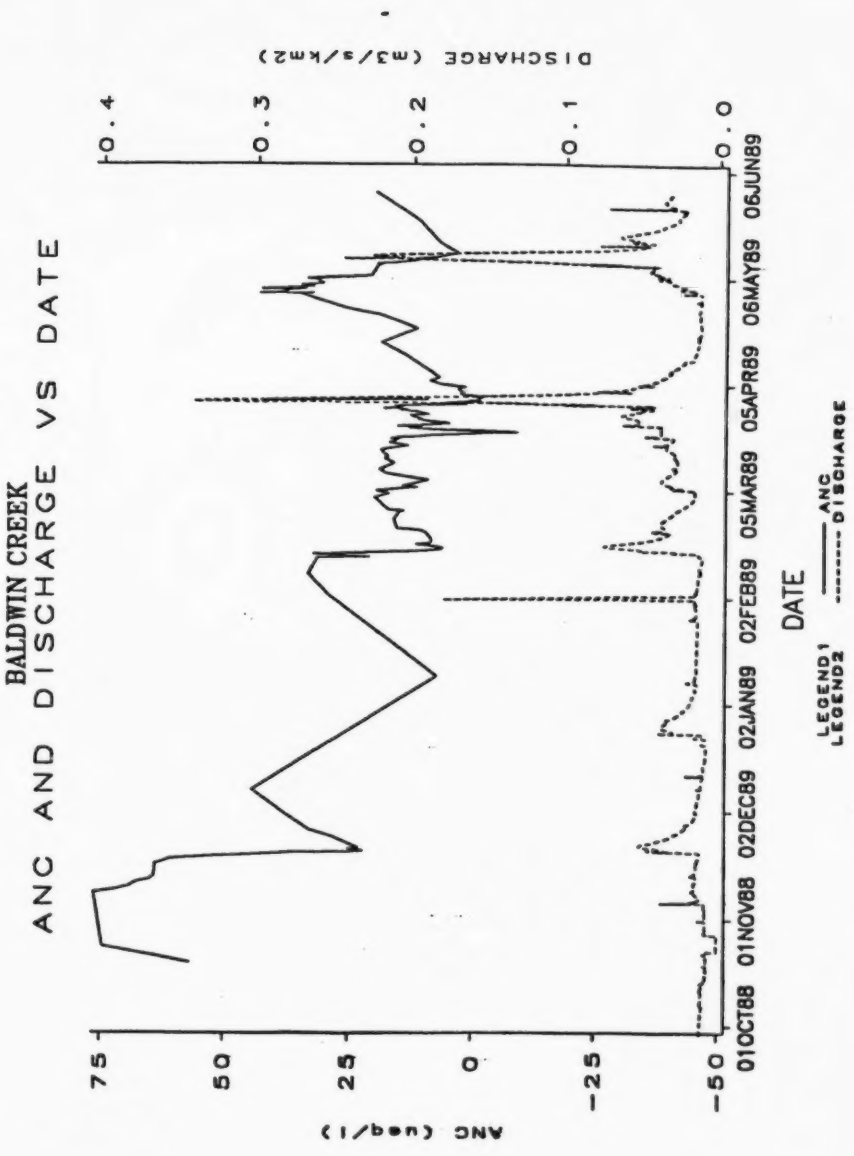


Figure 23. ANC and discharge variations for Baldwin Creek for October 1988 to June 1989.

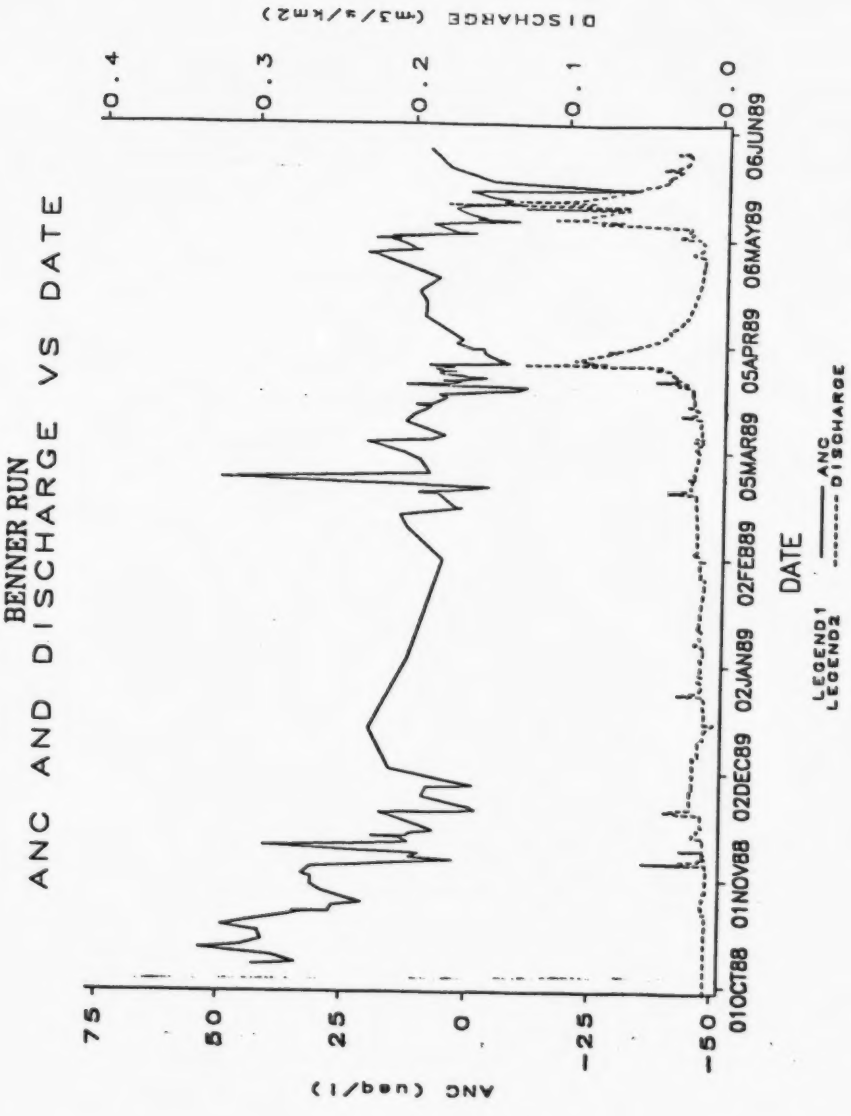


Figure 24. ANC and discharge variations for Benner Run for October 1988 to June 1989.

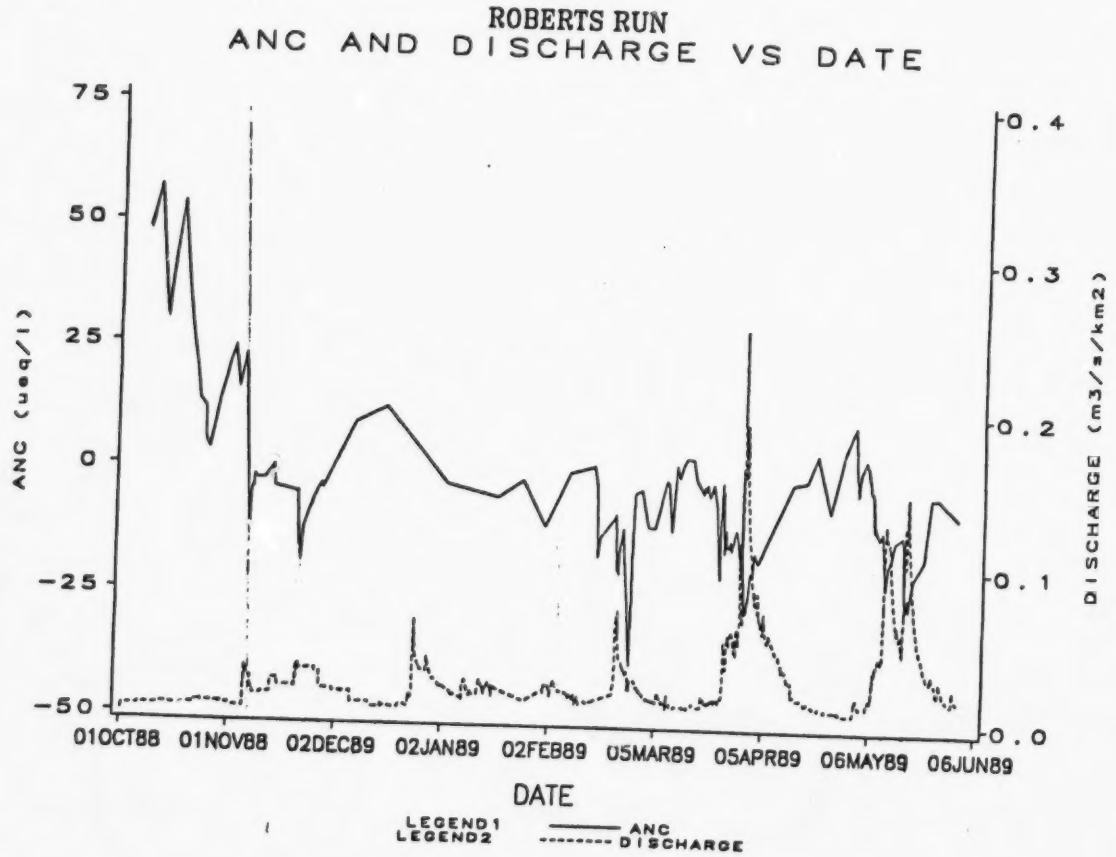


Figure 25. ANC and discharge variations for Roberts Run for October 1988 to June 1989.

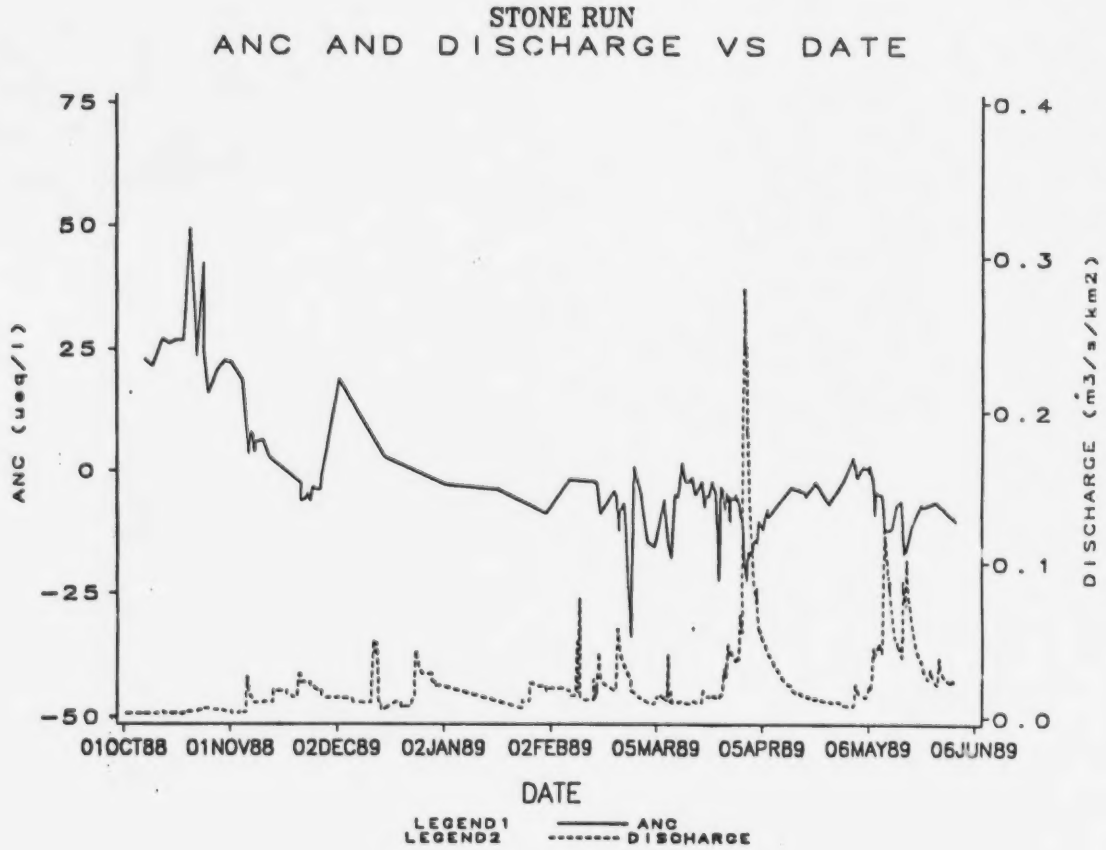


Figure 26. ANC and discharge variations for Stone Run for October 1988 to June 1989.

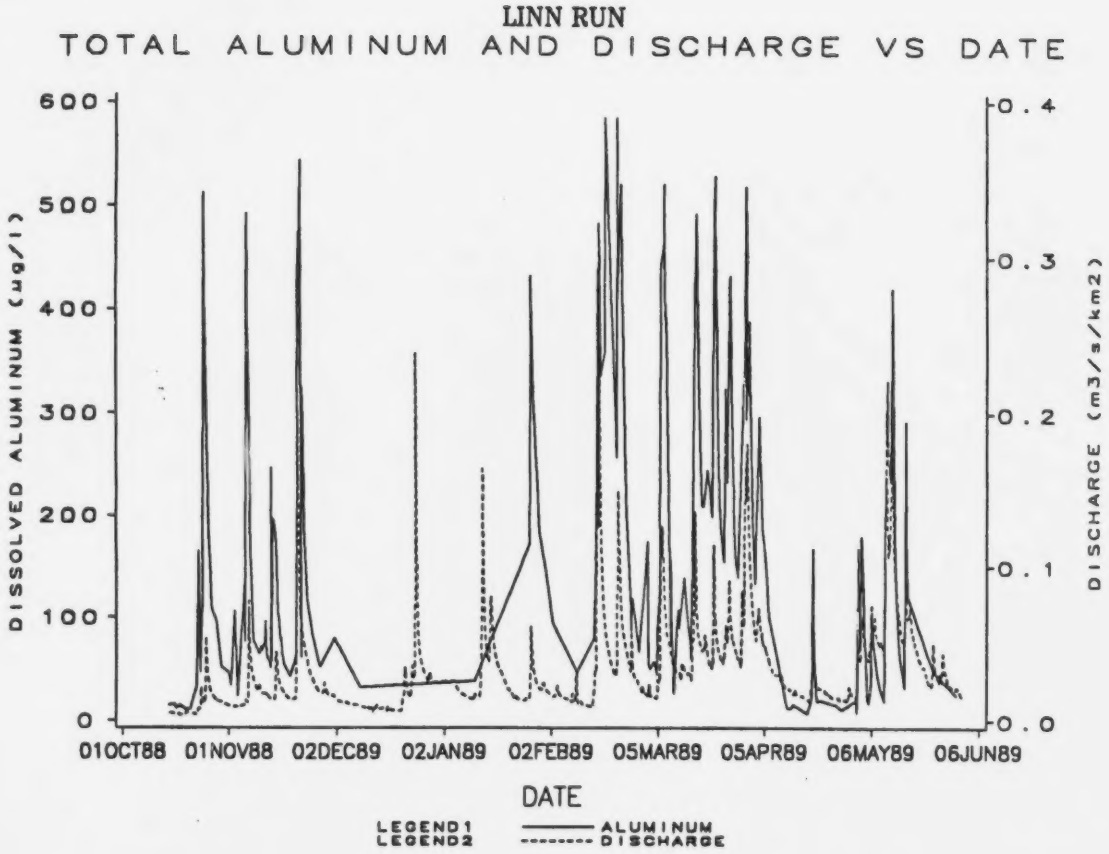


Figure 27. Aluminum and discharge variations for Linn Run for October 1988 to June 1989.

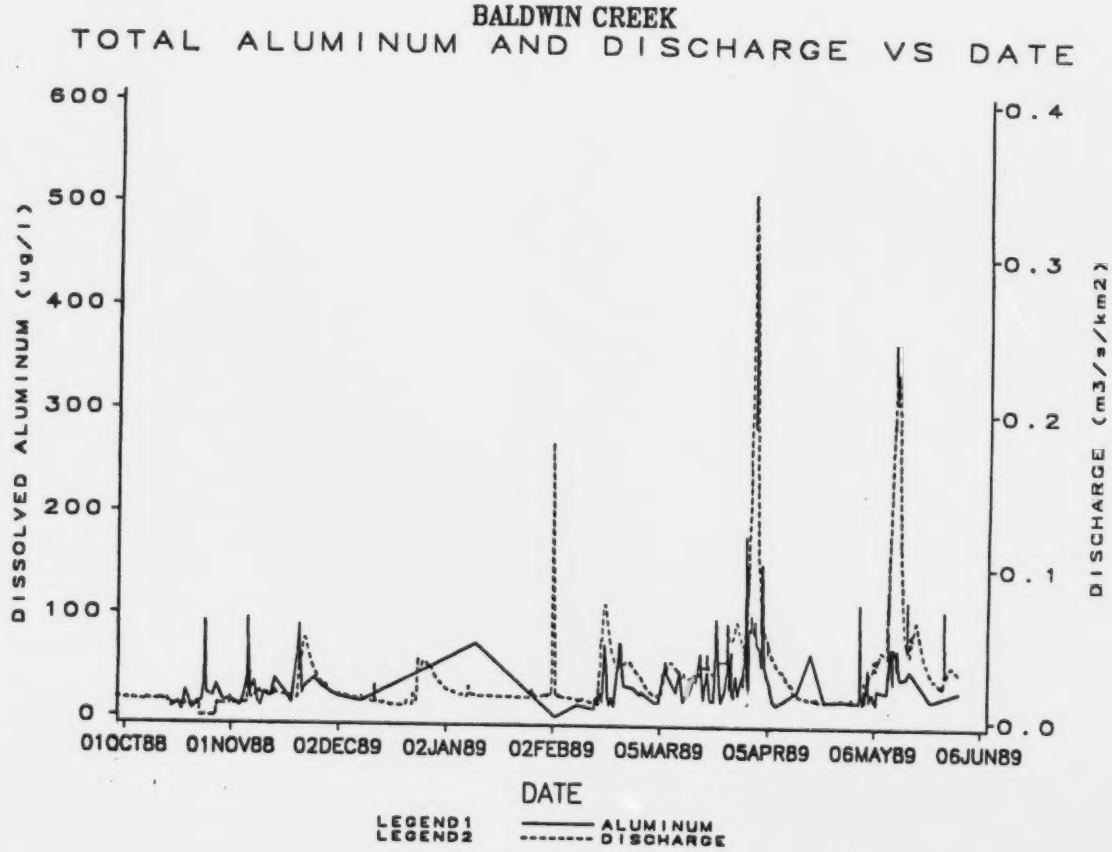


Figure 28. Aluminum and discharge variations for Baldwin Creek for October 1988 to June 1989.

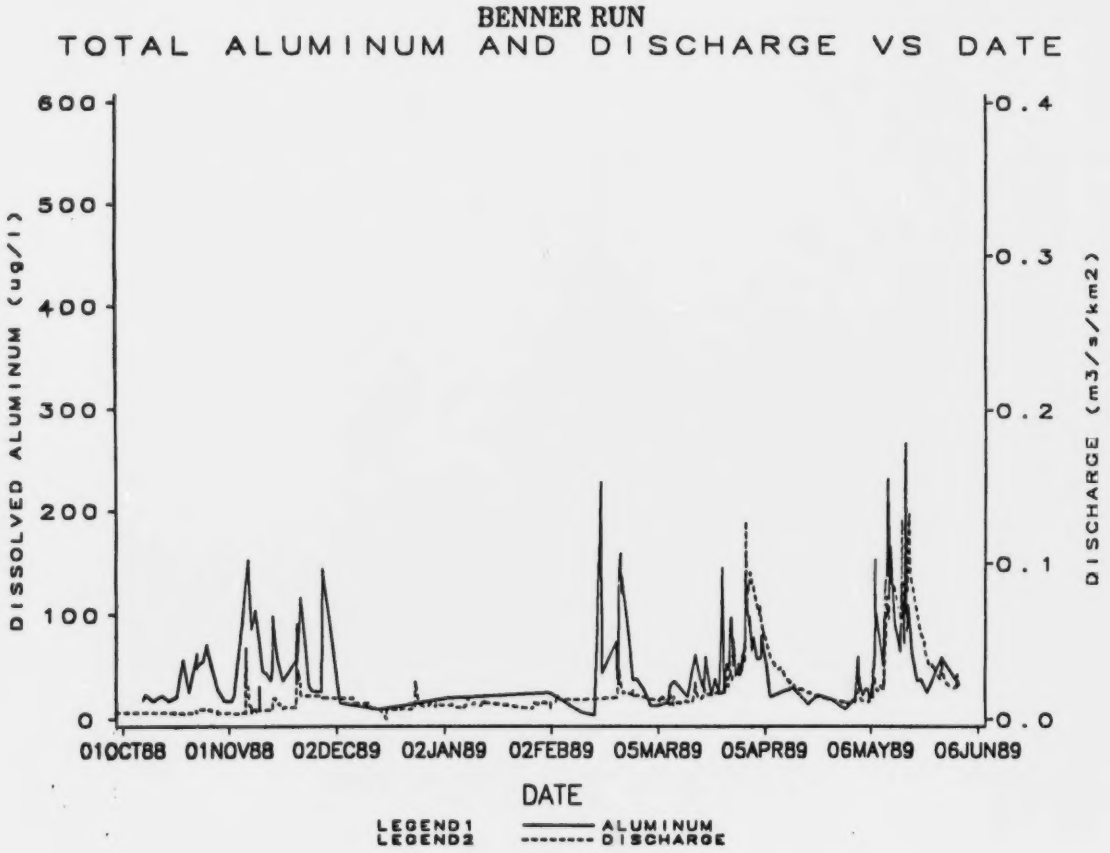


Figure 29. Aluminum and discharge variations for Benner Run for October 1988 to June 1989.

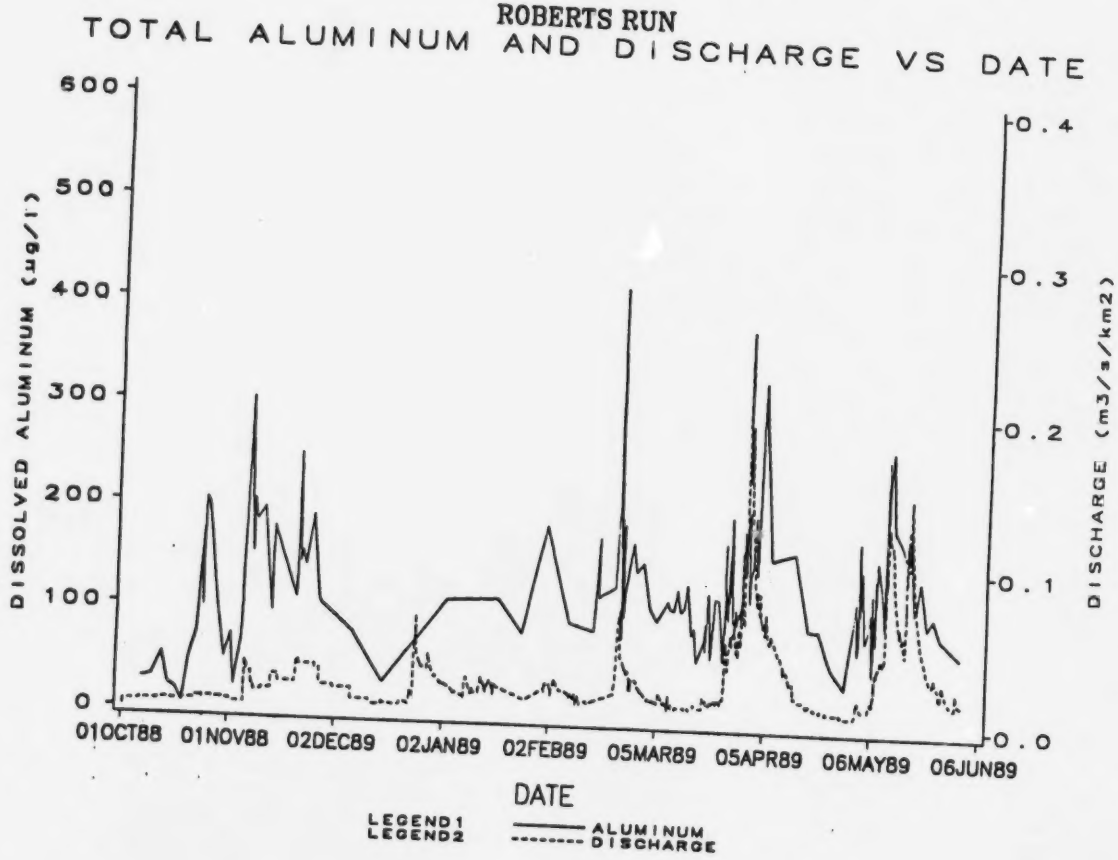


Figure 30. Aluminum and discharge variations for Roberts Run for October 1988 to June 1989.

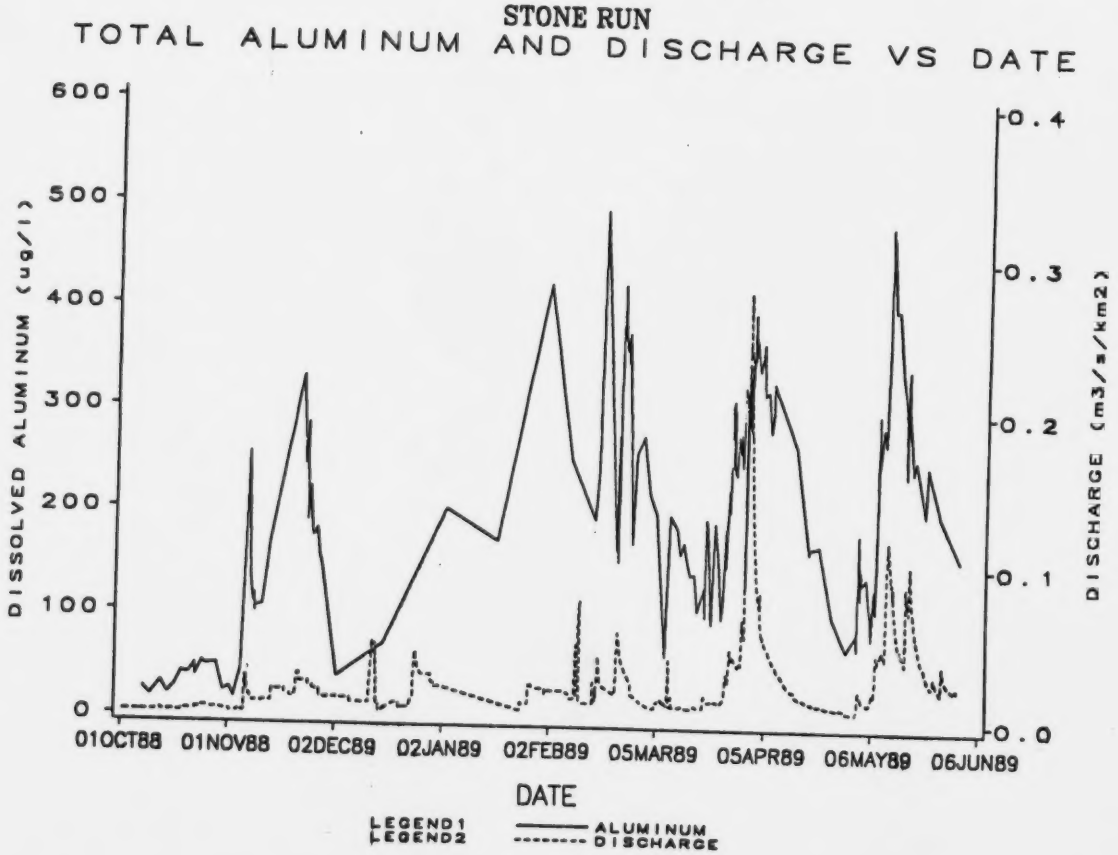


Figure 31. Aluminum and discharge variations for Stone Run for October 1988 to June 1989.

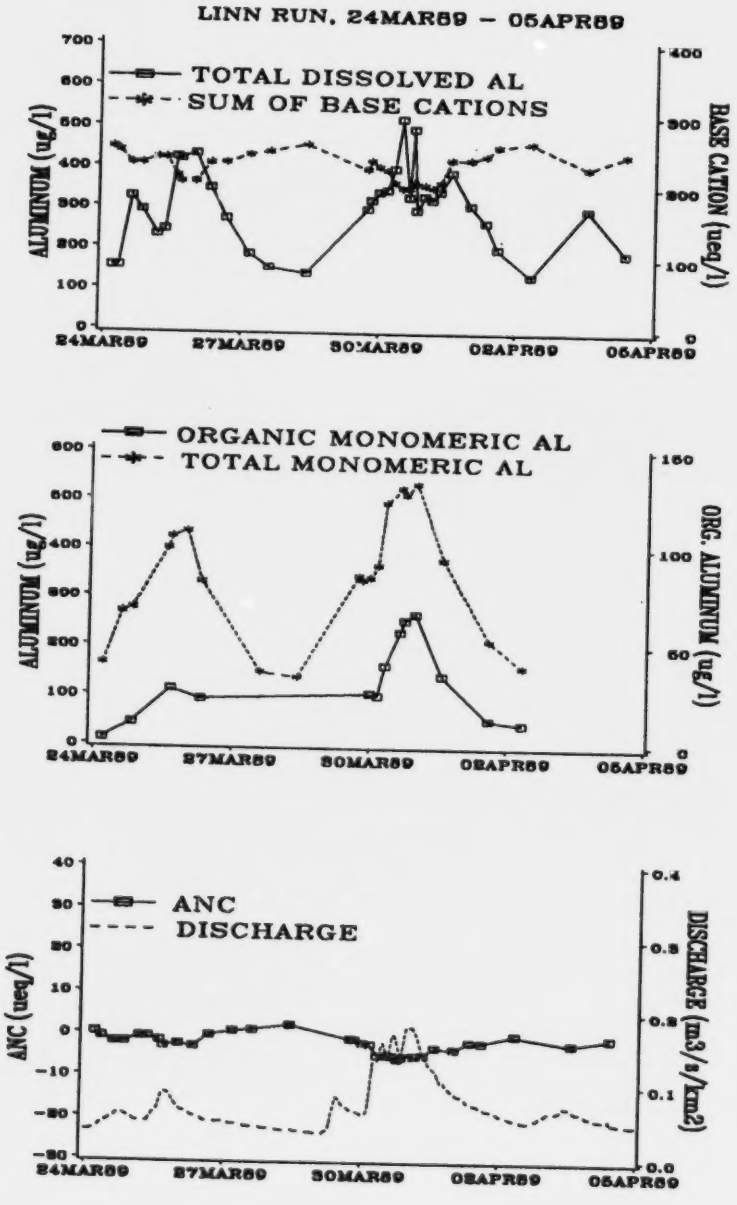


Figure 32. Episodic ANC, Al, cation chemistry for Linn Run for 24 March to 5 April, 1989.

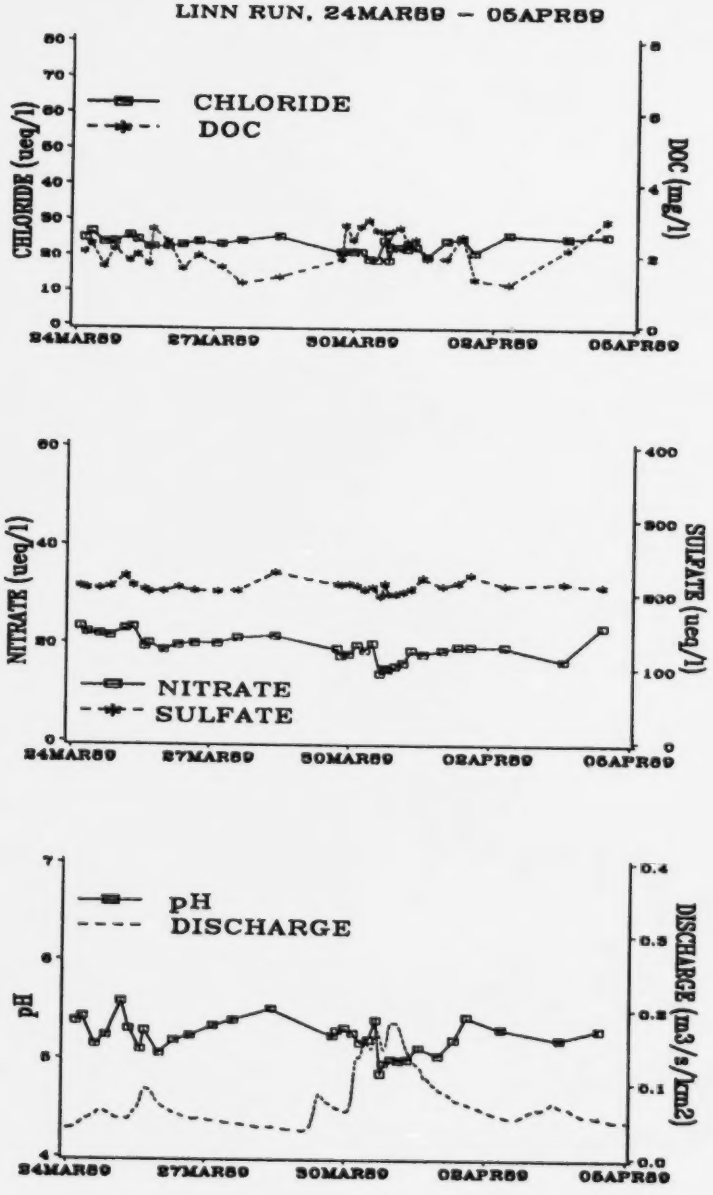


Figure 33. Episodic pH and anion chemistry for Linn Run for 24 March to 5 April, 1989.

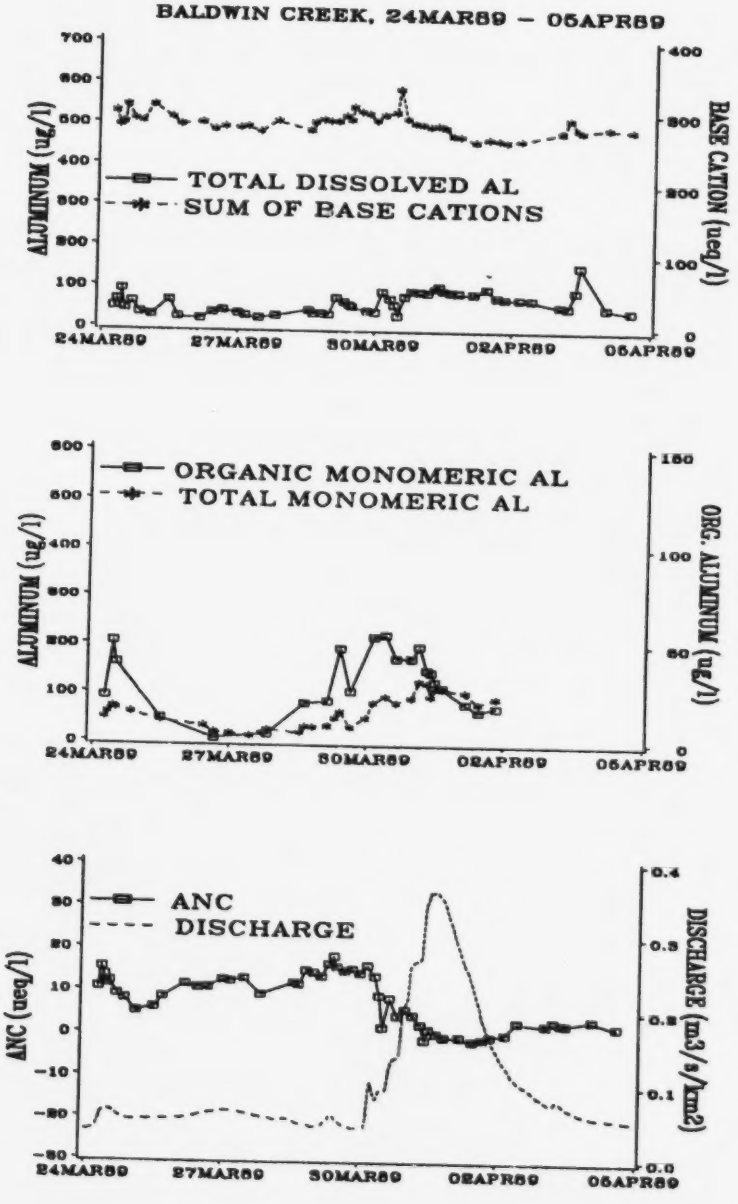


Figure 34. Episodic ANC, Al and cation chemistry for Baldwin Creek for 24 March to 5 April, 1989.

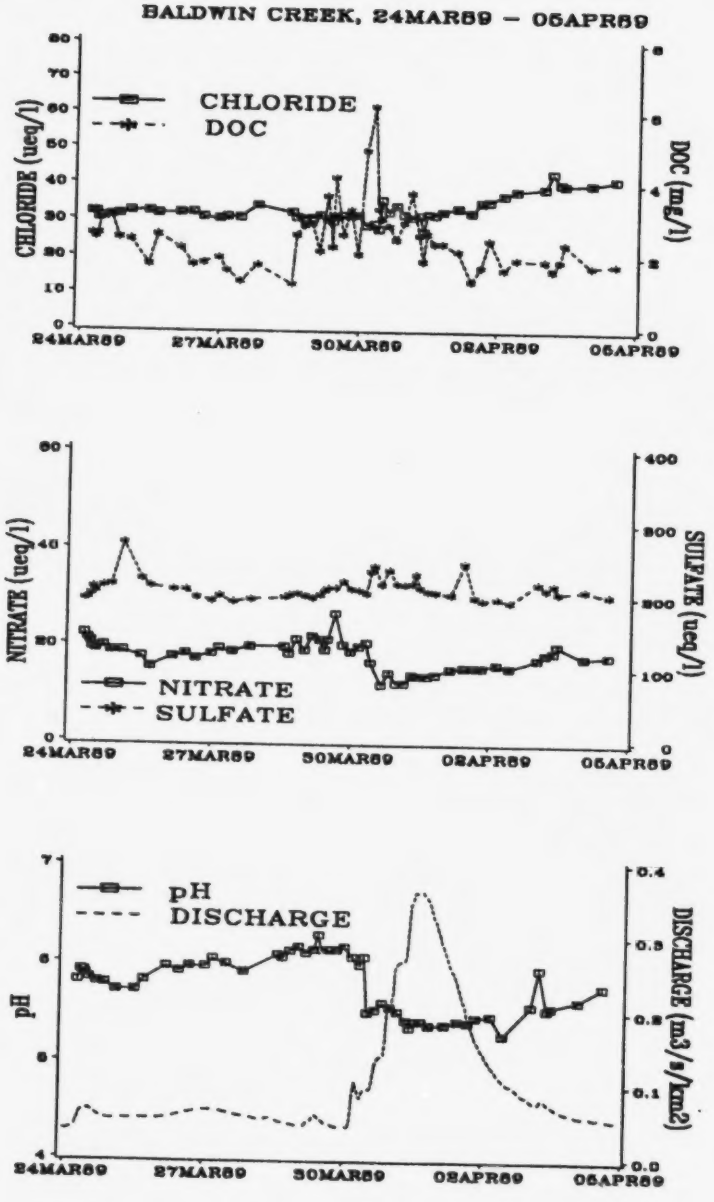


Figure 35. Episodic pH and anion chemistry for Baldwin Creek for 24 March to 5 April, 1989.

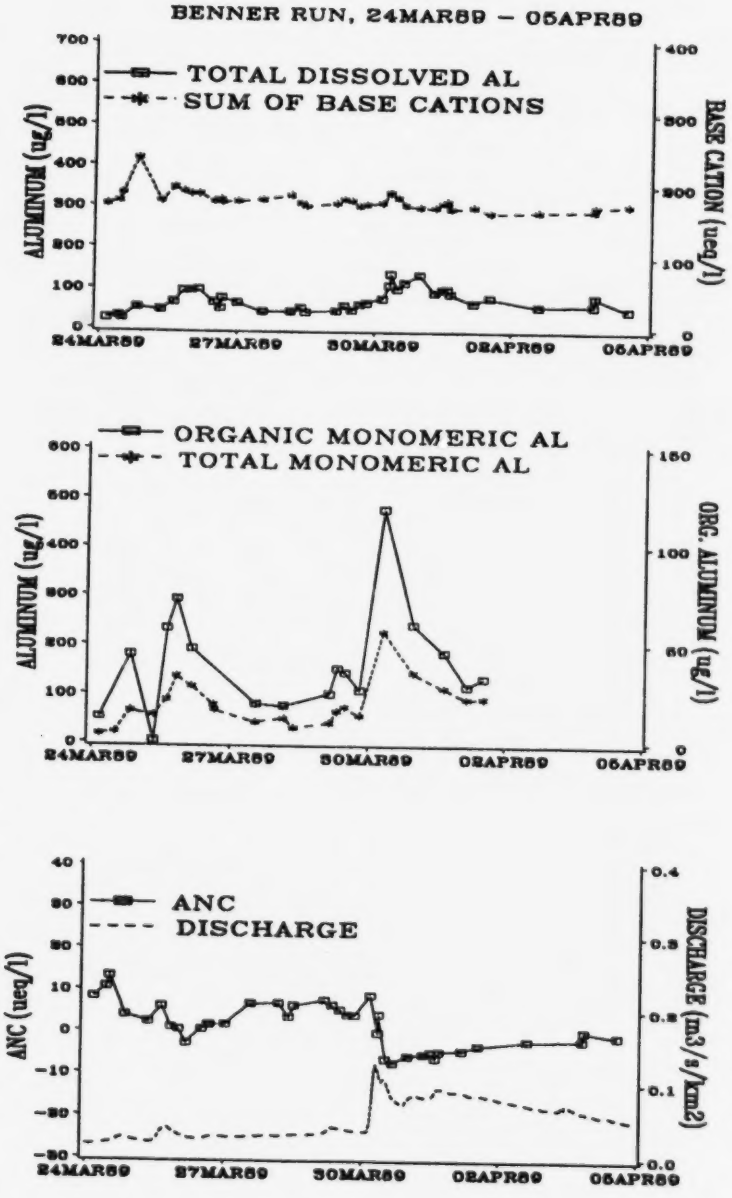


Figure 36. Episodic ANC, Al and cation chemistry for Benner Run for 24 March to 5 April, 1989.

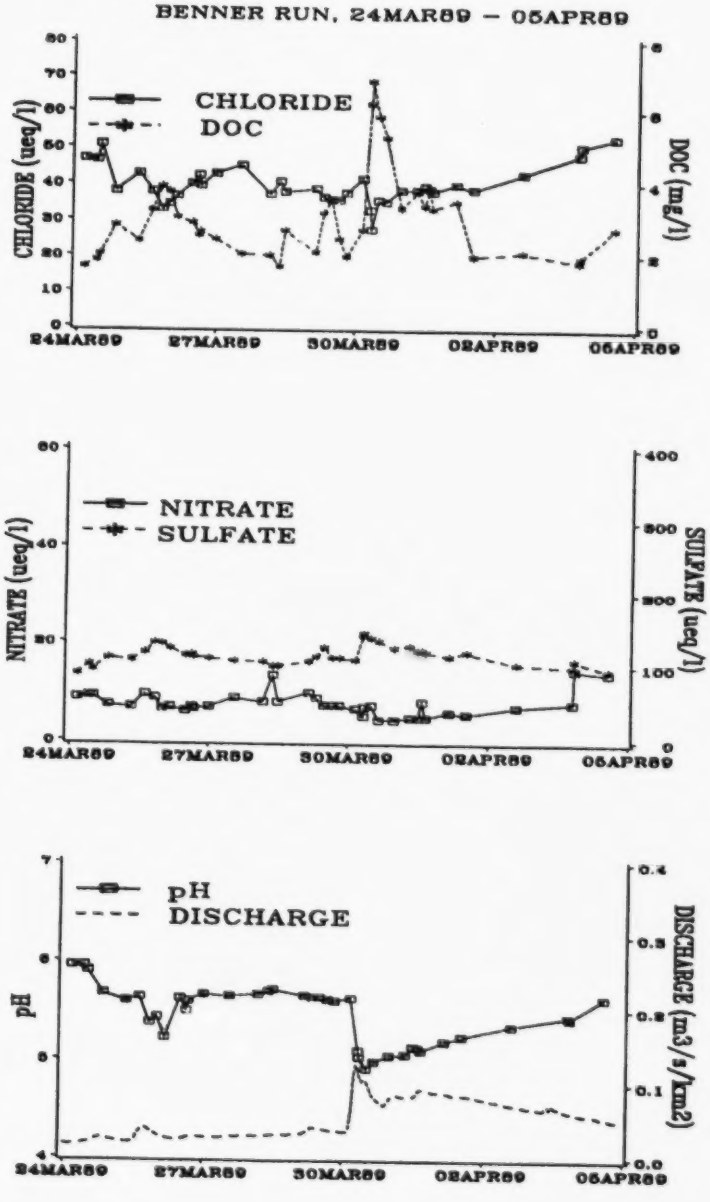


Figure 37. Episodic pH and anion chemistry for Benner Run for 24 March to 5 April, 1989.

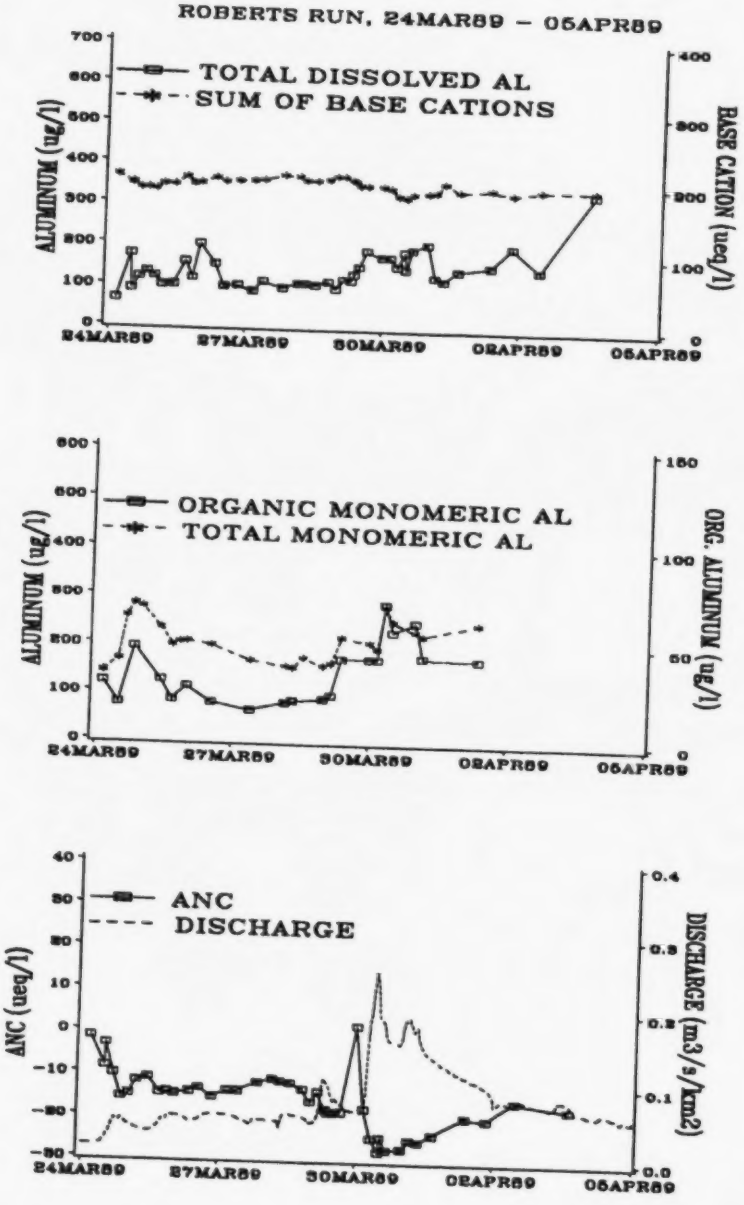


Figure 38. Episodic ANC, Al and cation chemistry for Roberts Run for 24 March to 5 April, 1989.

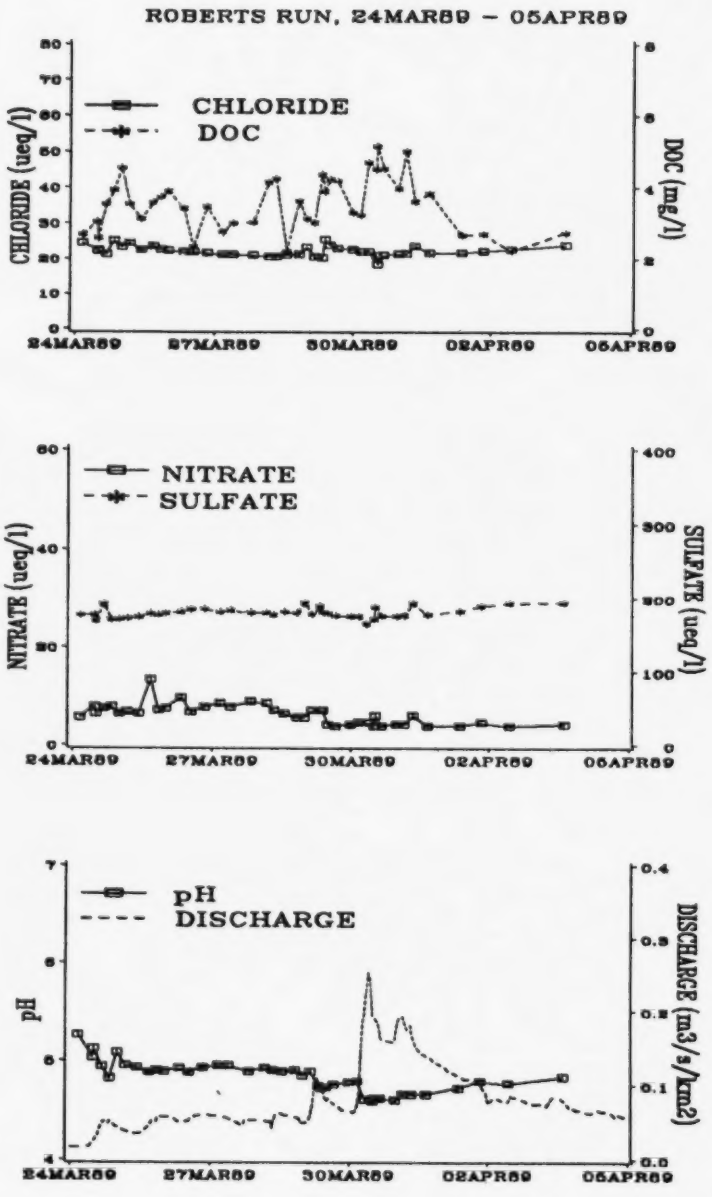


Figure 39. Episodic pH and anion chemistry for Roberts Run for 24 March to 5 April, 1989.

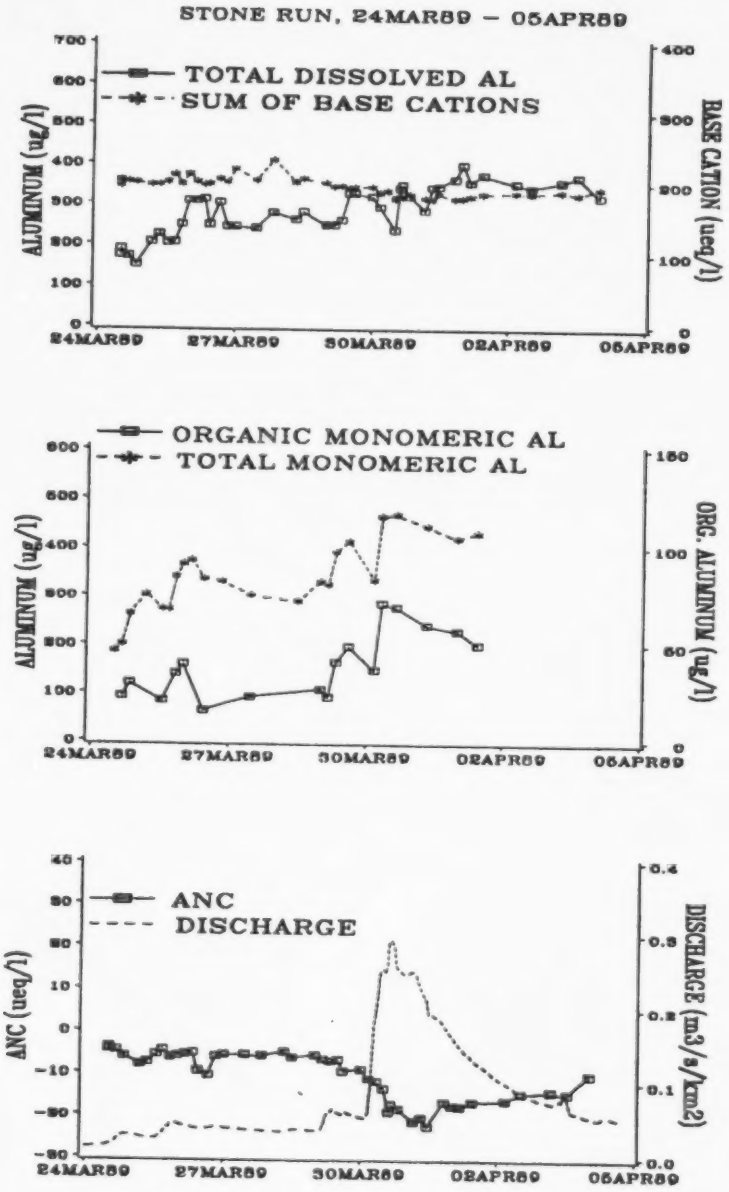


Figure 40. Episodic ANC, Al and cation chemistry for Stone Run for 24 March to 5 April, 1989.

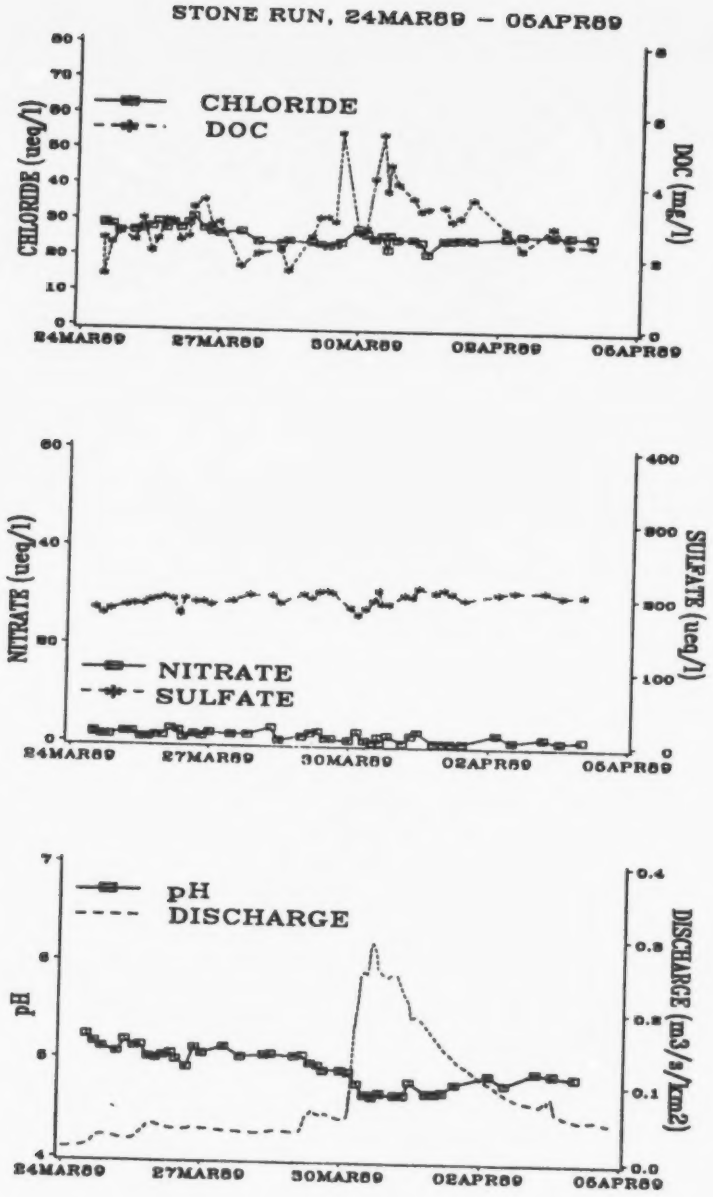


Figure 41. Episodic pH and anion chemistry for Stone Run for 24 March to 5 April, 1989.

show no consistent trends over time during the episodes. Total and organic monomeric Al show increases with flow on all streams during these events. Response during the May events (Figures 42-51) is quite similar to that in March-April, but Cl and sum of base cations tend to show dilution effects during peak flow and NO_3 increases late in the event on the falling limb of the hydrograph.

A review of episodic data for the October 1988 to June 1989 period showed that pH changes during events expressed as μeq/L were greatest on Linn Run and least on Baldwin Run. Maximum H^+ change for an event appeared to be a better index to episodic severity than mean H^+ change. Based upon maximum H^+ change, a ranking of streams from most to lease severe episodes is:

Linn > Stone > Roberts > Benner > Baldwin.

Fish mortality in surface waters affected by acidic deposition has been attributed to high concentrations of dissolved aluminum (Al), and controlled studies have confirmed that the inorganic monomeric species of Al is toxic to fish. Monomeric Al includes organic monomeric Al and inorganic monomeric species. Inorganic monomeric Al includes free Al plus Al-hydroxide, fluoride and sulfate complexes. The ERP measures the monomeric Al species in streams during periods of high streamflow and during fish studies.

Total monomeric Al and organic monomeric Al are measured directly on stream samples, and inorganic monomeric Al is measured by the difference between total and organic monomeric Al. Total monomeric Al is measured on an aliquot of filtered sample by rapid chelation with hydroxyquinoline and extraction into an organic solvent, methyl iso-butyl ketone. The extracts containing monomeric Al are measured by visible spectroscopy. Organic monomeric Al is measured by the same technique except the filtered sample is first passed through a cation-exchange column to isolate organic Al.

Monomeric Al was measured on over 300 ERP samples from the 5 Pennsylvania streams from Fall 1988 to Spring 1989. Total monomeric Al and inorganic monomeric Al increased with decreasing stream pH on all 5 streams, but each stream showed a different response to pH. In general, total dissolved Al measurements were quite similar to total monomeric Al measurements. Linn Run showed the most dramatic increase in total monomeric Al and inorganic monomeric Al with decreasing pH and increasing streamflow compared to the other streams. The highest concentration of total monomeric Al on Linn Run was approximately 0.75 mg/L at pH 4.7. Monomeric Al on Stone, Roberts and Benner Runs also increased with decreasing pH and increasing streamflow, showing maximum concentrations of total monomeric Al of 0.475 mg/L, 0.35 mg/L and 0.25 mg/L, respectively. Baldwin Creek had maximum total monomeric Al levels of less than 0.1 mg/L and did not show significant decreases in pH like the other streams did. The varying response of the streams to pH is partly due to differences in mineral composition between the watershed and varying contact times with these minerals. Monomeric Al levels on all streams are a minimum at pH around 6, indicating some control by the mineral gibbsite. Additional analyses of monomeric Al versus pH will be made in order to determine which minerals control the streams. Organic monomeric levels increased with increasing streamflow on all streams, but levels were much lower than inorganic Al. Organic monomeric Al was a signficant part of total monomeric Al on Benner Run and Baldwin Creek for all streamflows and on the

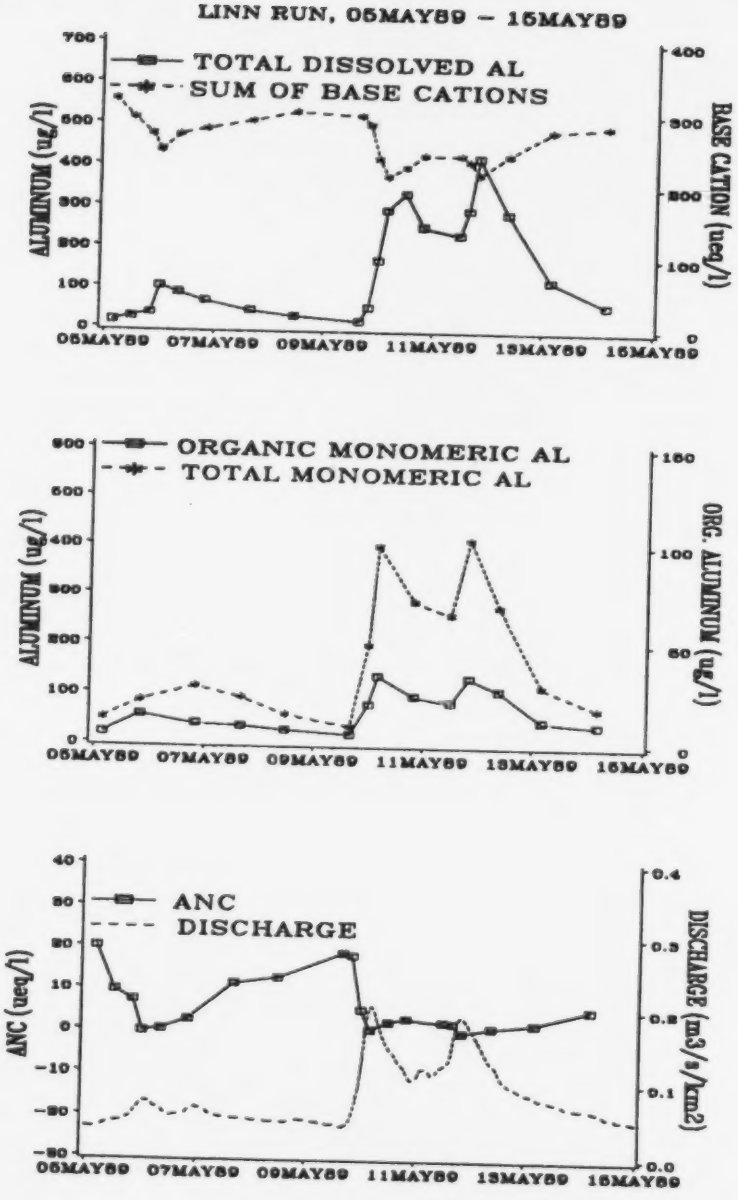


Figure 42. Episodic ANC, Al and cation chemistry for Linn Run for 5 to 15 May, 1989.

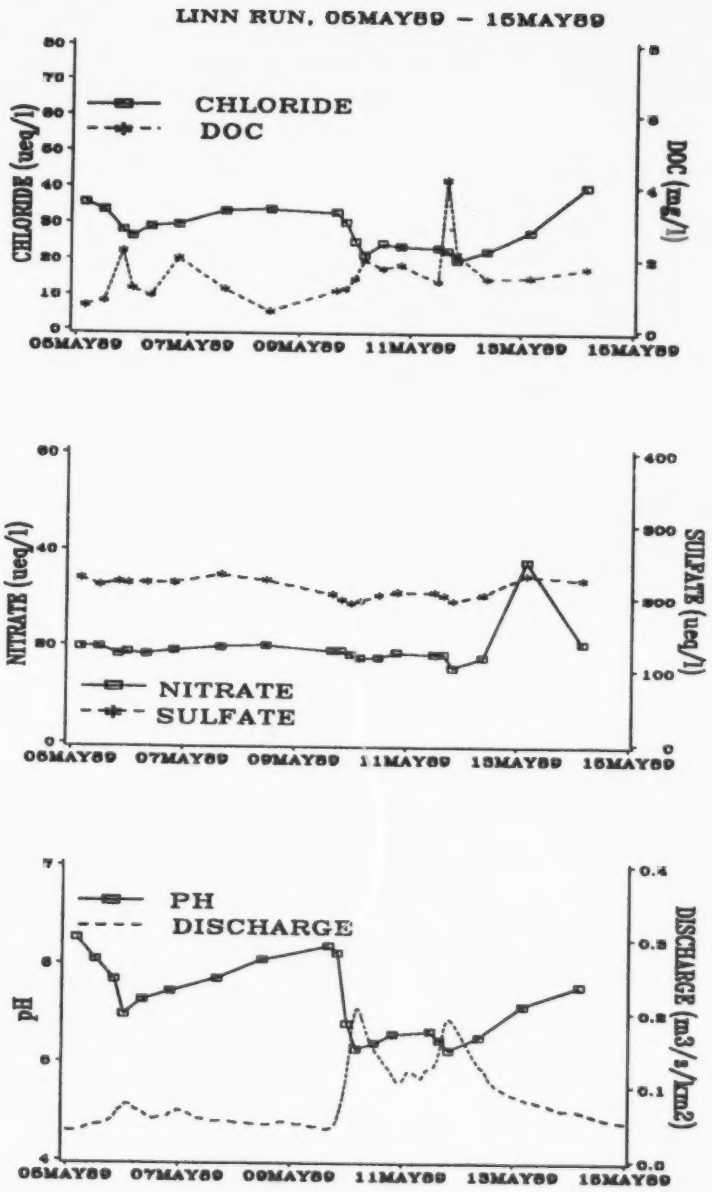


Figure 43. Episodic pH and anion chemistry for Linn Run for 5 to 15 May, 1989.

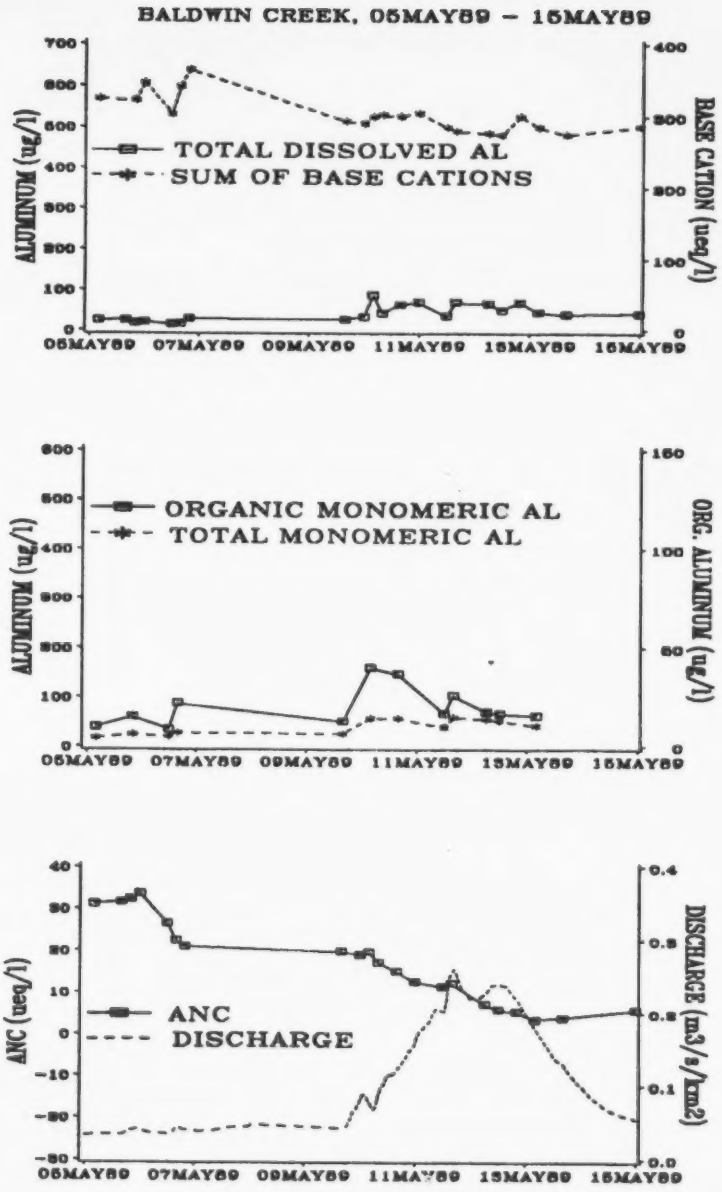


Figure 44. Episodic ANC, Al, and cation chemistry for Baldwin Creek for 5 to 15 May, 1989.

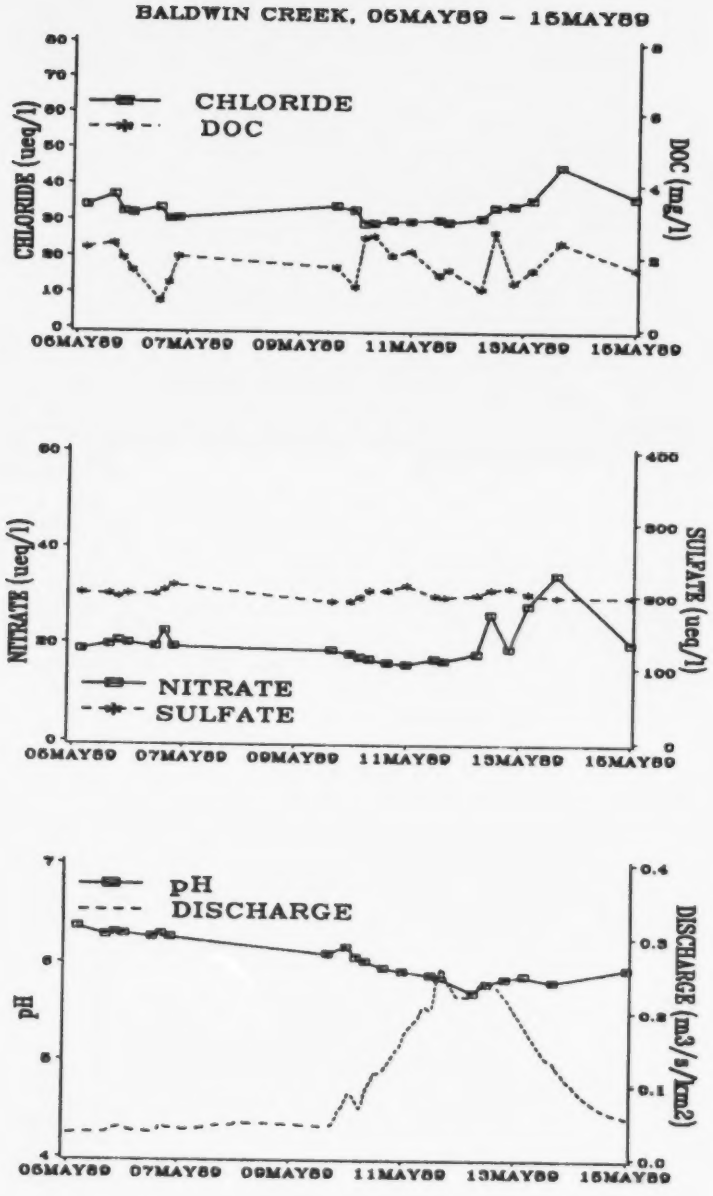


Figure 45. Episodic pH and anion chemistry on for Baldwin Creek for 5 to 15 May, 1989.

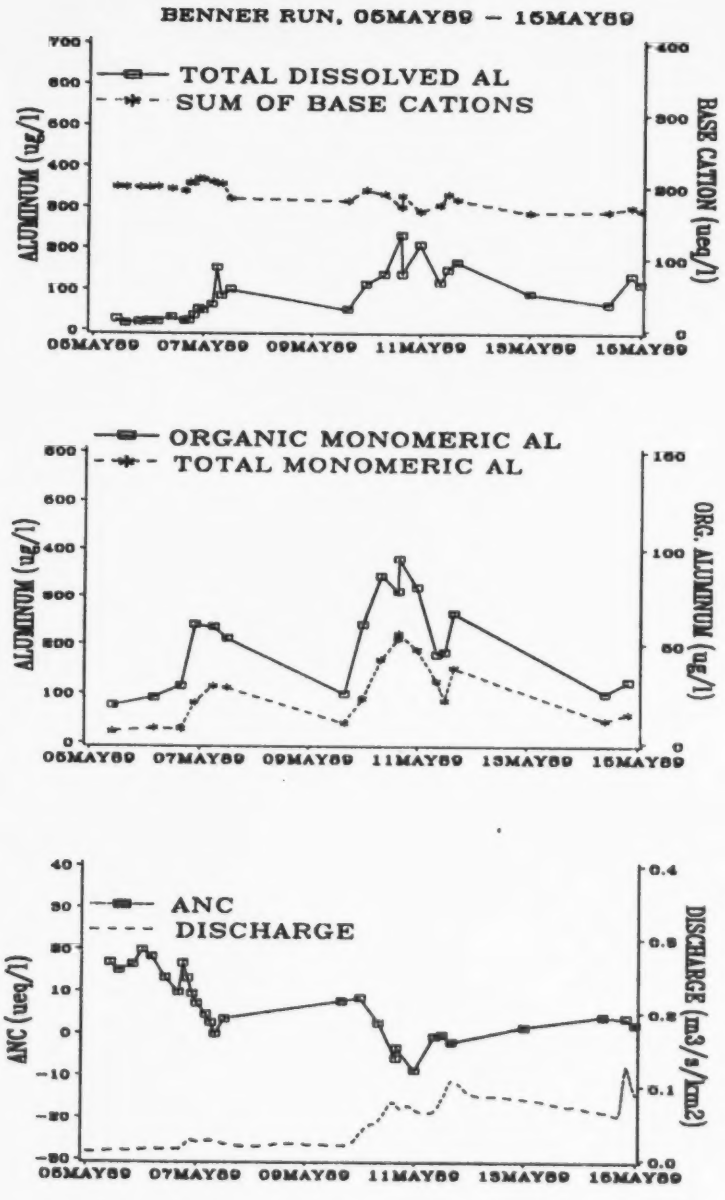


Figure 46. Episodic ANC, Al and cation chemistry for Benner Run for 5 to 15 May, 1989.

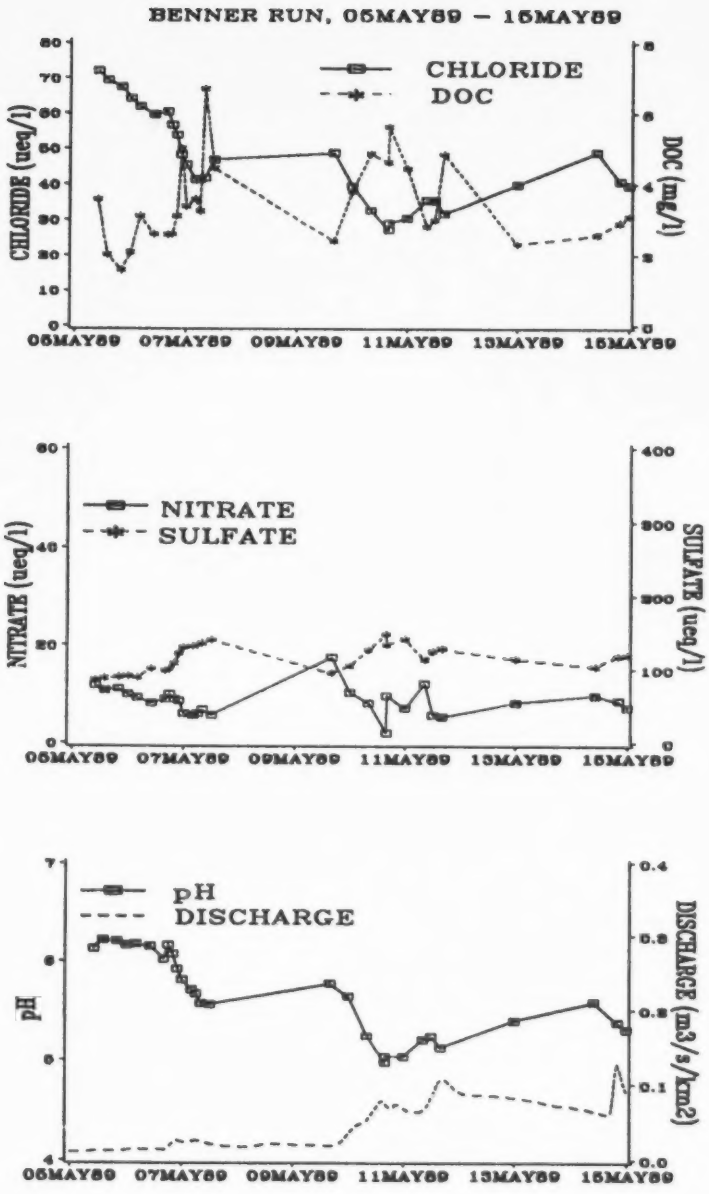


Figure 47. Episodic pH and anion chemistry for Benner Run for 5 to 15 May, 1989.

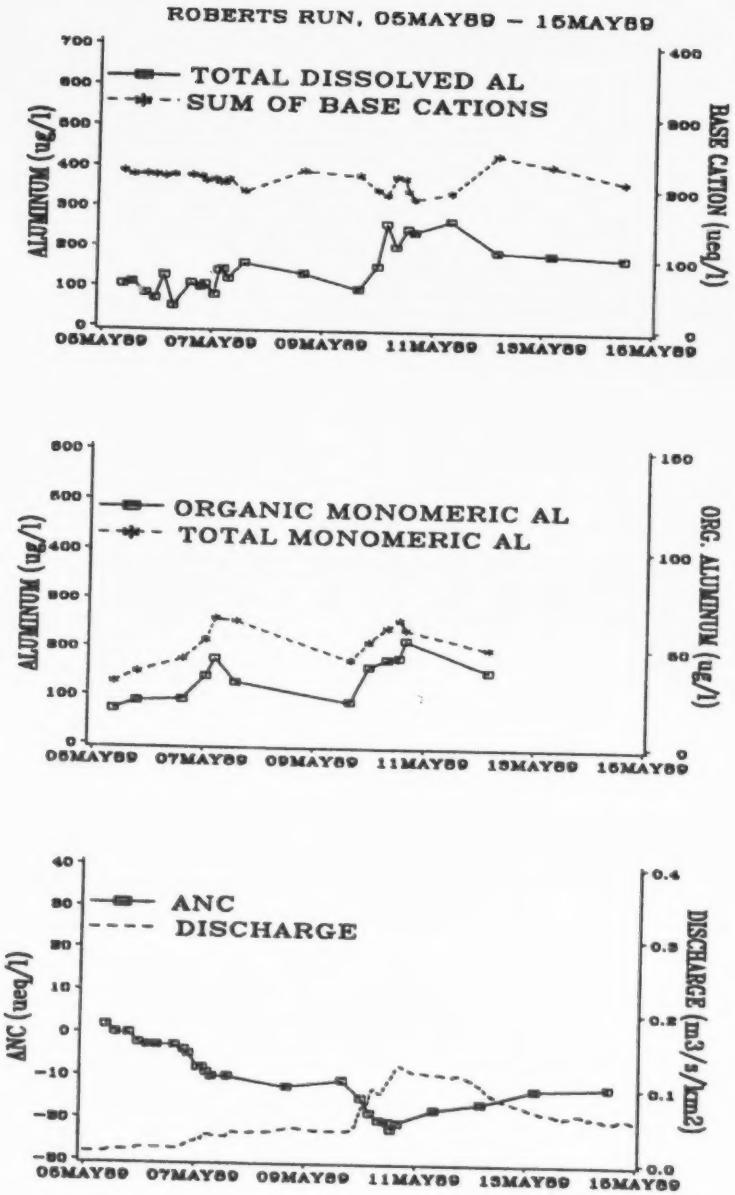


Figure 48. Episodic ANC, Al, and cation chemistry for Roberts Run for 5 to 15 May, 1989.

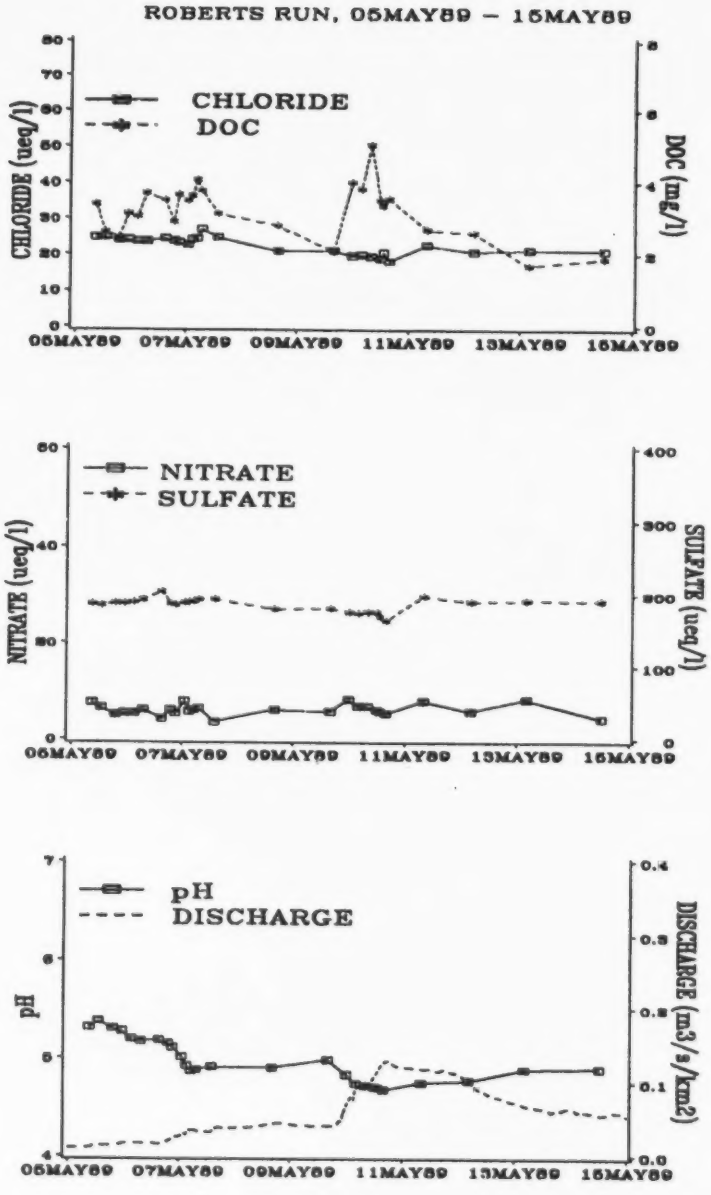


Figure 49. Episodic pH and anion chemistry for Roberts Run for 5 to 15 May, 1989.

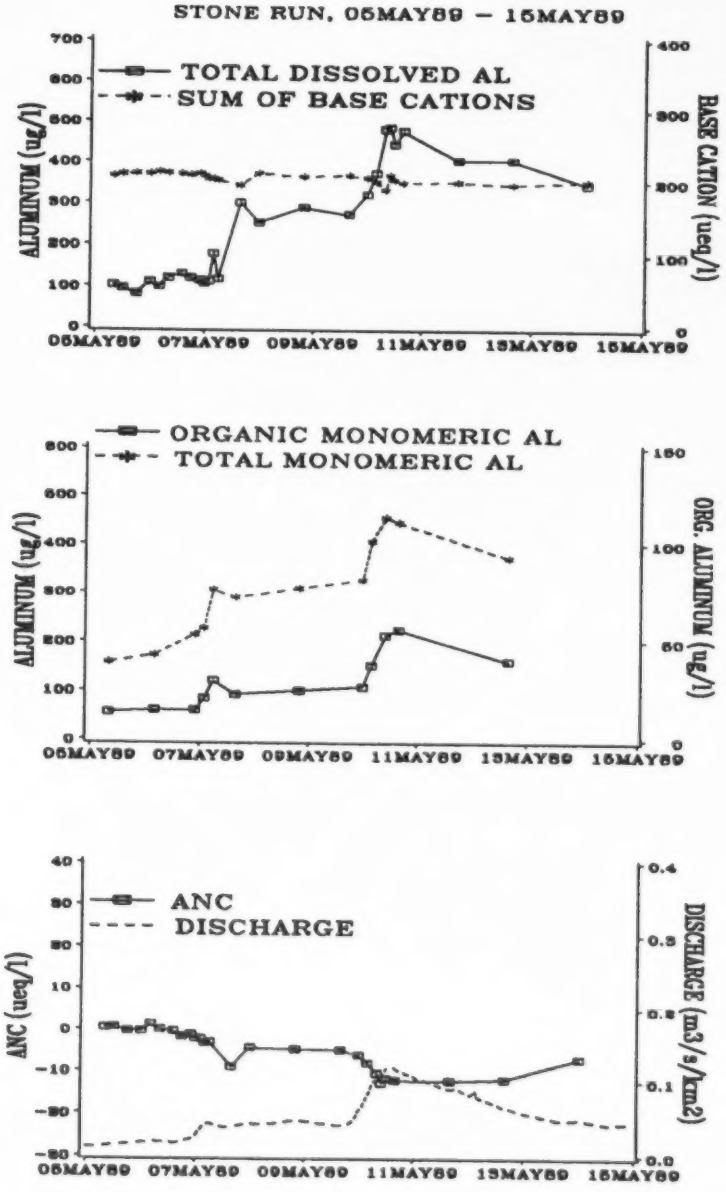


Figure 50. Episodic ANC, Al and cation chemistry for Stone Run for 5 to 15 May, 1989.

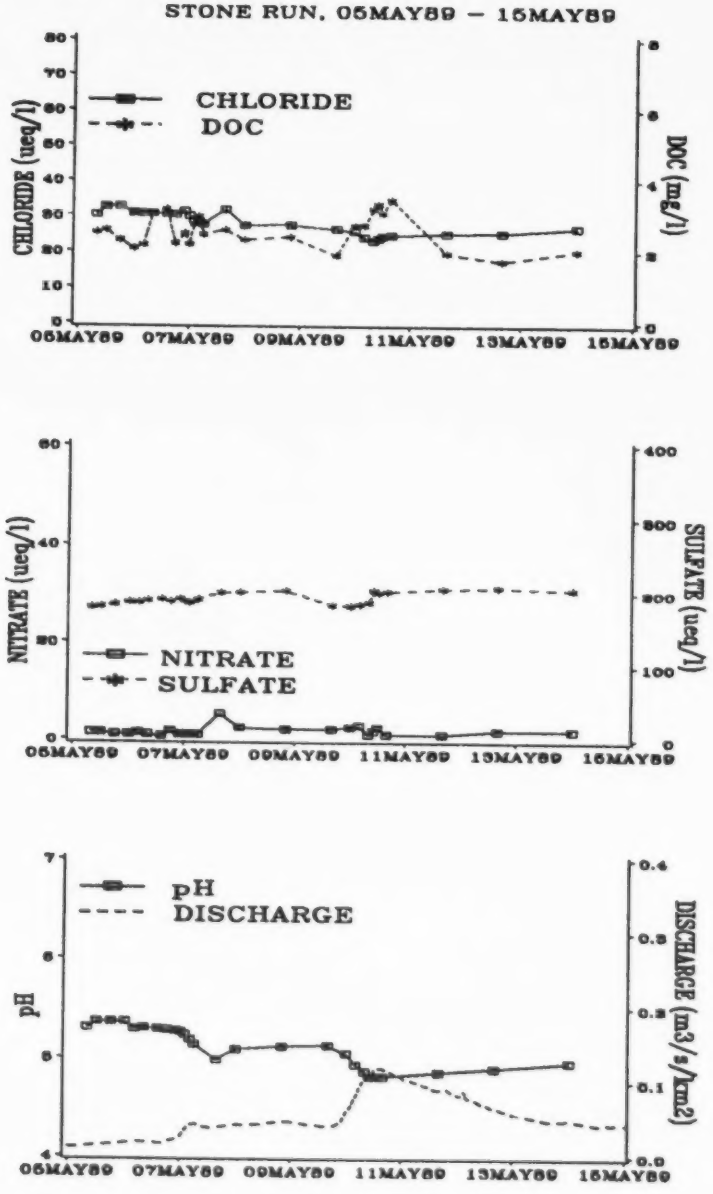


Figure 51. Episodic pH and anion chemistry for Stone Run for 5 to 15 May, 1989.

other streams during low flow conditions. Additional samples will be analyzed for monomeric Al speciation during Fall 1989 and Spring 1990.

FISHERIES

Chronic acidification of rivers and streams has resulted in extinction of fish populations (Sharpe et al., 1984; Hesthagen, 1986; Haines and Baker, 1986). Episodes of acidification have caused substantial mortality of fish in field bioassays (Harvey et al., 1982; Sharpe et al., 1983; Gunn and Keller, 1984; Johnson et al., 1987; Gagen and Sharpe, 1987). Mortality of free-ranging adult fish during acid episodes has been observed in several lotic waters of Scandinavia and North America (Hesthagen, 1986; Harvey and McArdle, 1986; and Gagen et al., 1989). The mechanism of population loss in acidified waters is generally thought to be high mortality during early life history stages (Gunn, 1986); however, computer simulations have shown that high annual morality of adult fish could prove even more detrimental to recruitment than mortality during early life stages (Van Winkle et al., 1986). Furthermore, yearling and adult fish may be less tolerant of acidification than young-of-the-year fish based on in-situ bioassays (Johnson et al., 1987).

Fish populations may respond to acid episodes behaviorally by moving to microhabitats of lower acidity. While trout movement in response to acid episodes has been observed in field studies (Gagen and Sharpe, 1987), the importance of avoidance behavior to wild populations requires further research.

The objective of the present study was to determine the effect of short-term acid runoff episodes on stream fish populations. We have concentrated our efforts on field studies including (1) in-situ bioassays of native brook trout (Salvelinus fontinalis) and native sculpins (Cottus bairdi and C. cognatus), (2) radio tracking of brook trout, and (3) abundance estimates of brook trout populations which were marked and set to known densities. Fisheries response was compared among five streams representing a wide range of episode severity. Responses were also compared within each stream among seasons with greater and lesser episode severity. Figures 52 and 53 outline the timing of field studies on each stream relative to the changes in discharge.

Fish communities in the study streams are composed of few species. Wild brook trout populations were present in each of the study streams (Table 5). The two streams with the highest pH and lowest dissolved aluminum concentrations also supported wild sculpin populations in the vicinity of our continuous monitors (Table 5). A few brown trout were found near the monitor on Benner Run.

While most of our study has been conducted near the monitoring site of each stream, the spatial variation in water chemistry and fish communities throughout each stream drainage should also be considered.

Species richness of fish communities is typically lower in the lower order (smaller) streams of drainage networks (Horwitz, 1978). Spatial and temporal variation in hydrologic regime and chemical parameters appear to explain these fish community patterns in certain cases (Horwitz, 1978 and Matthews and Styron, 1981). Schofield and Driscoll (1987) concluded that fish species

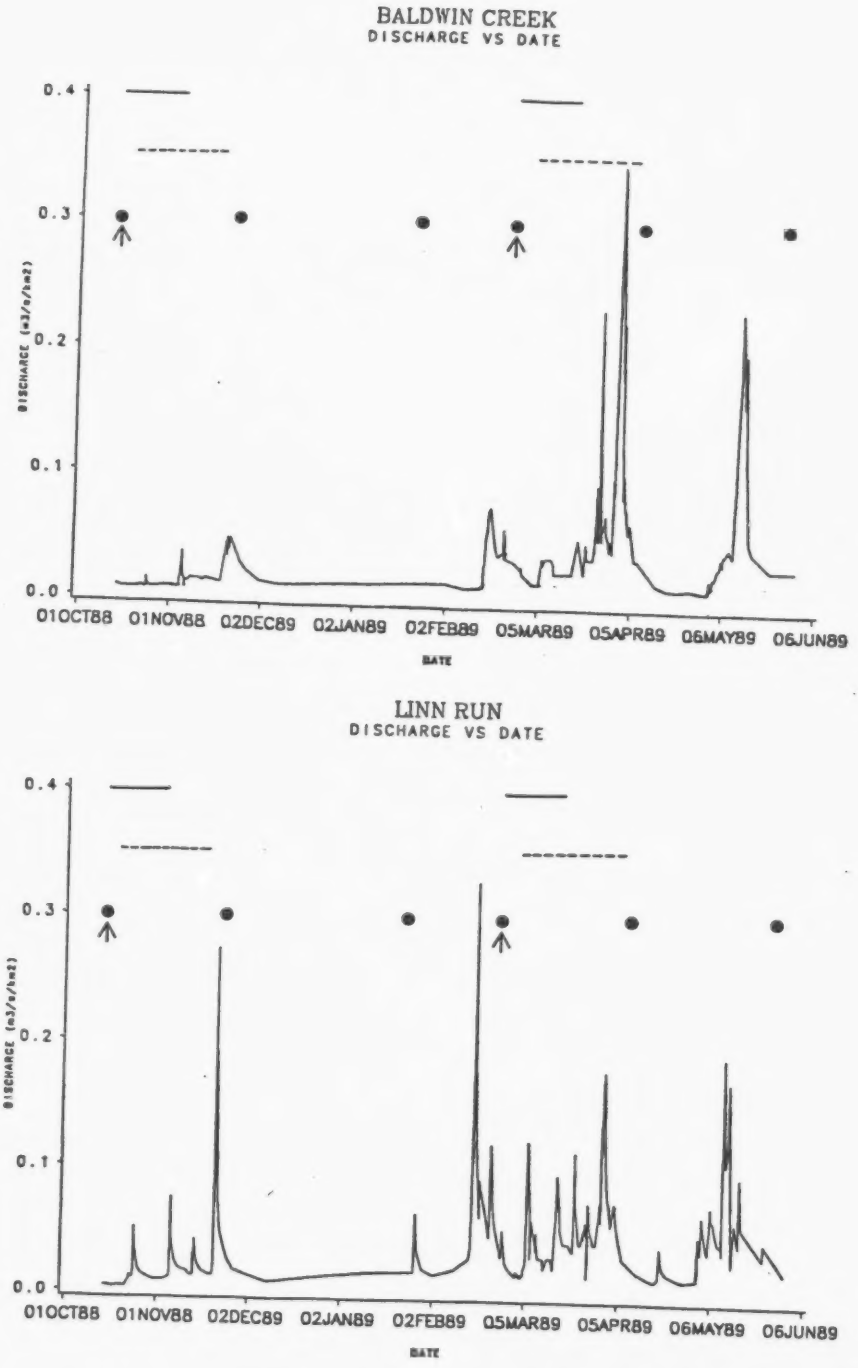


Figure 52. Fisheries sampling activities and stream discharge on Linn Run and Baldwin Creek from October 1988 to June 1989. Arrows indicate when brook trout density was set to 75/0.1 ha, solid circles indicate times of population estimates, solid horizontal bars show bioassay periods, and broken horizontal bars show telemetry periods.

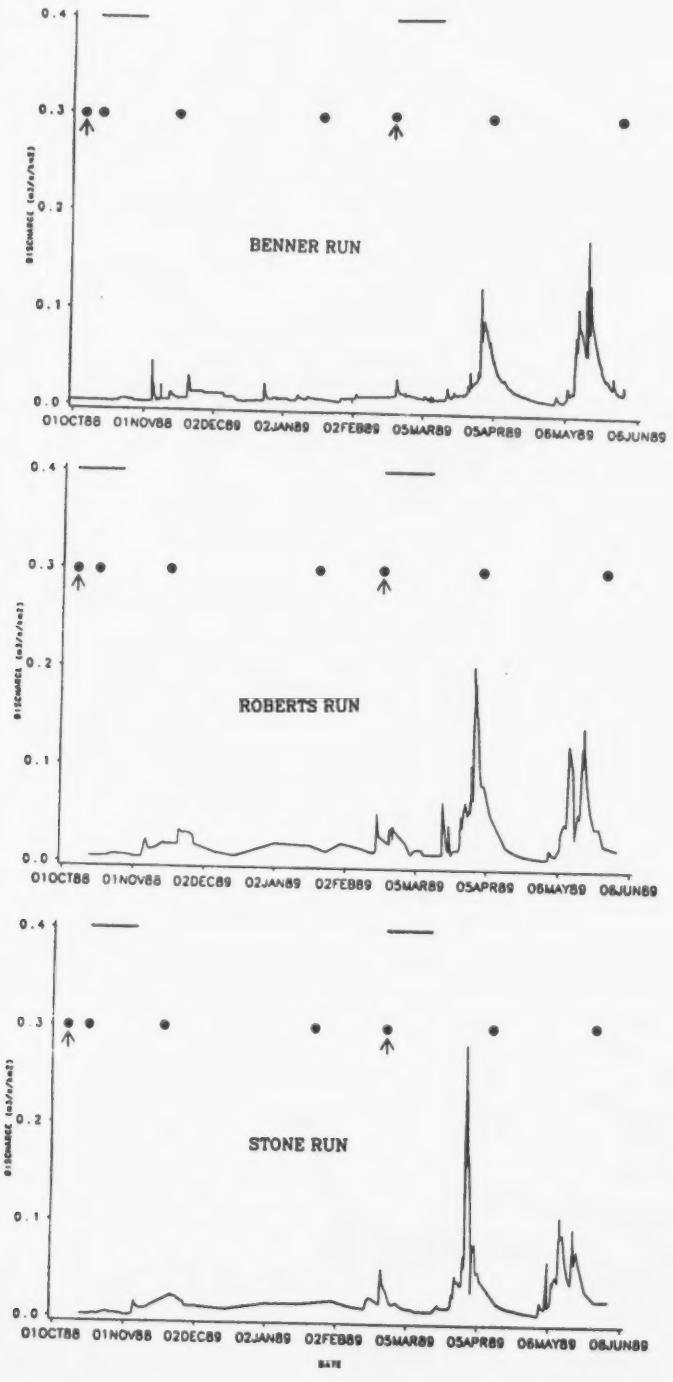


Figure 53. Fisheries sampling activities and stream discharge on Benner, Roberts, and Stone Runs from October 1988 to June 1989. Arrows indicate when brook trout density was set to 75/0.1 ha, solid circles indicate times of population estimates, and solid horizontal bars show bioassay periods.

TABLE 5

Summary of Fish Communities in the 200m Transplant Sites During Initial Surveys from October 4 to 13, 1988 and Characterization of pH and Total Dissolved Aluminum in Each Study Stream from October 1988 to June 1989

	Linn Run	Stone Run	Roberts Run	Benner Run	Baldwin Creek
Estimated brook trout density, #/0.1 ha	22	228	164	224	173
95% confidence interval	(22,23)	(221,236)	(159,170)	(221,230)	(168,181)
Estimated brook trout density, g/m^2	0.73	2.74	2.46	3.61	2.42
Total catch #/0.1 ha					
Brook trout	22	221	159	221	168
Slimy sculpin	0	0	0	311	0
Mottled sculpin	0	0	0	0	89
Brown trout	0	0	0	48	0
Baseflow chemistry, medians for all grab samples					
pH	5.76	5.21	5.31	5.95	6.34
Aluminum, µg/L	94	186	111	34	24
Number of samples	86	85	83	80	91
Episode chemistry for ISCO and grab samples, 10th percentile pH and 90th percentile Al					
pH	5.03	4.79	4.70	5.12	5.75
Aluminum, µg/L	436	368	196	123	86
Number of samples	280	231	216	195	246

distribution patterns in the North Branch of the Moose River were largely determined by relative physiological tolerances of fish species and gradients of pH and aluminum within the drainage network.

During May 1989 we collected samples from 4 to 6 sites within each of the five study streams to characterize gradients in pH and total dissolved aluminum concentration. Fish communities show lower species richness in the headwater portions of each drainage (Figures 54-58). No fish were found in the extreme headwaters except in Benner Run and Baldwin Creek where pH was higher and aluminum concentrations were lower than in the other three streams.

The study streams generally show lower aluminum concentrations and higher pH in the downstream portions of their drainages (Figures 54-58). This is presumably due to input of alkaline groundwater from seeps, springs, and spring fed tributaries. These more neutralized regions represent potential microhabitats available to fish populations which are sampled in our transplant sites near the continuous monitors. Furthermore, wild populations of fish in the drainage network potentially served as a source of immigrant fish to our transplant sites.

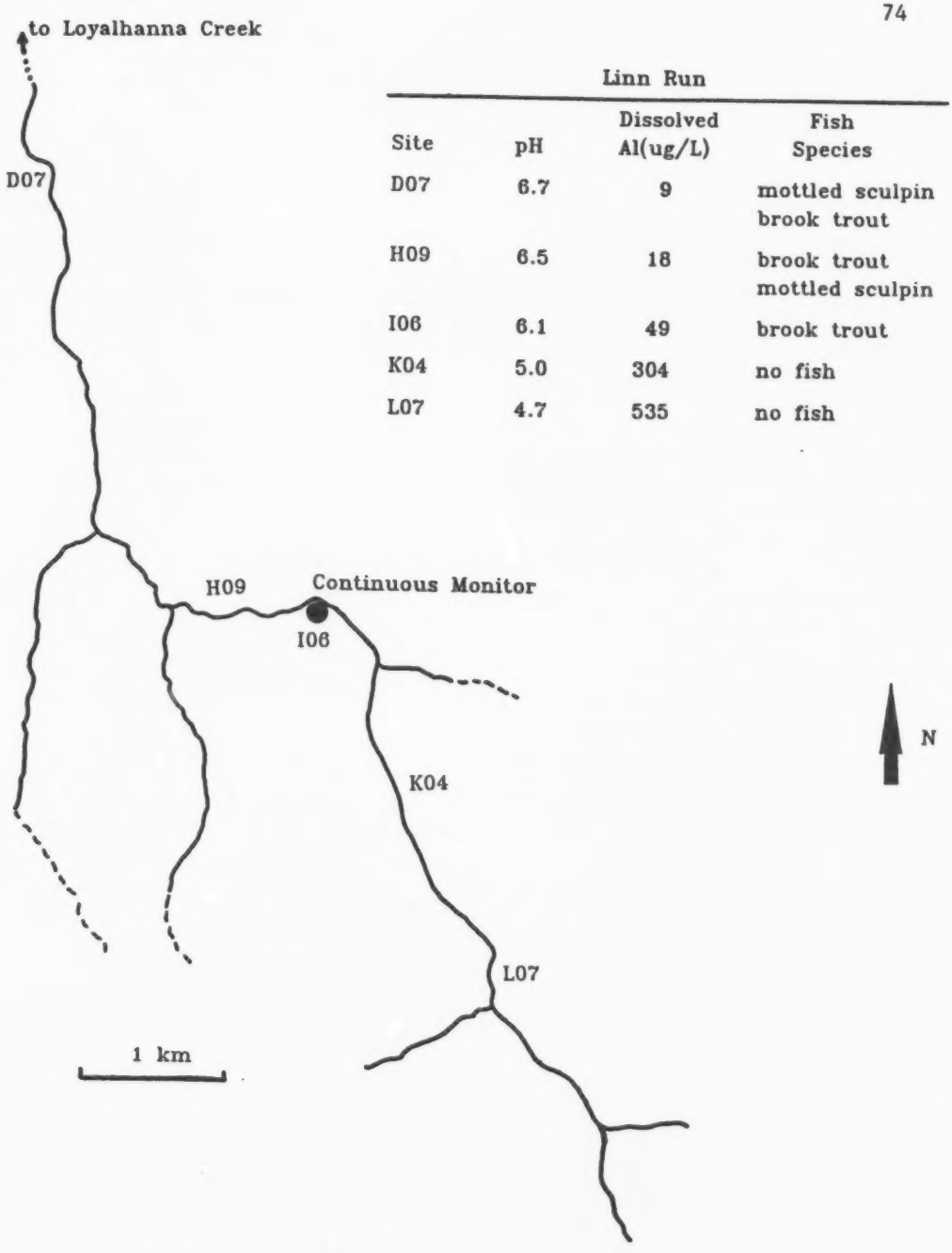
Bioassay Experiments

In-situ bioassays of wild brook trout, mottled sculpin, and slimy sculpin were conducted on all study streams during Fall 1988 and Spring 1989 near each gaging station at the mouth of the catchment. Linn Run and Baldwin Creek bioassays evaluated the toxicity of acid runoff episodes to brook trout and mottled sculpin while slimy sculpin and brook trout were used on Stone, Roberts and Benner Runs. Fall bioassays were conducted between October 6 and November 3, 1988. The Spring bioassays extended from February 22 to March 21, 1989. The bioassay period was not completely concurrent among streams; however, the majority of the bioassay period was concurrent among streams.

A total of 21 or more fish were used for each bioassay except Benner Run in Fall 1988 only had 16 fish. The number of fish in each jug was set at 7 for the Spring 1989 bioassays because of suspected crowding problems. We reported only the first 20d of the bioassays because the methodology did not assure survival in reference sites much longer than that.

During the Fall 1988 bioassay period, Linn Run (Figure 59) experienced a small runoff episode in response to incident precipitation. No other study streams experienced flow increases of any consequence. There was no significant mortality of bioassay fish on any of the study streams (Figures 59-63). Total dissolved aluminum reached toxic concentrations during the acid runoff episode on Linn Run; however, episode duration was not sufficient to cause significant mortality of bioassay fish. This finding verifies that fish can live in the stream water at each of the sites at least during low flow periods; thus, none of the stream sites are chronically acidified when bioassays were conducted.

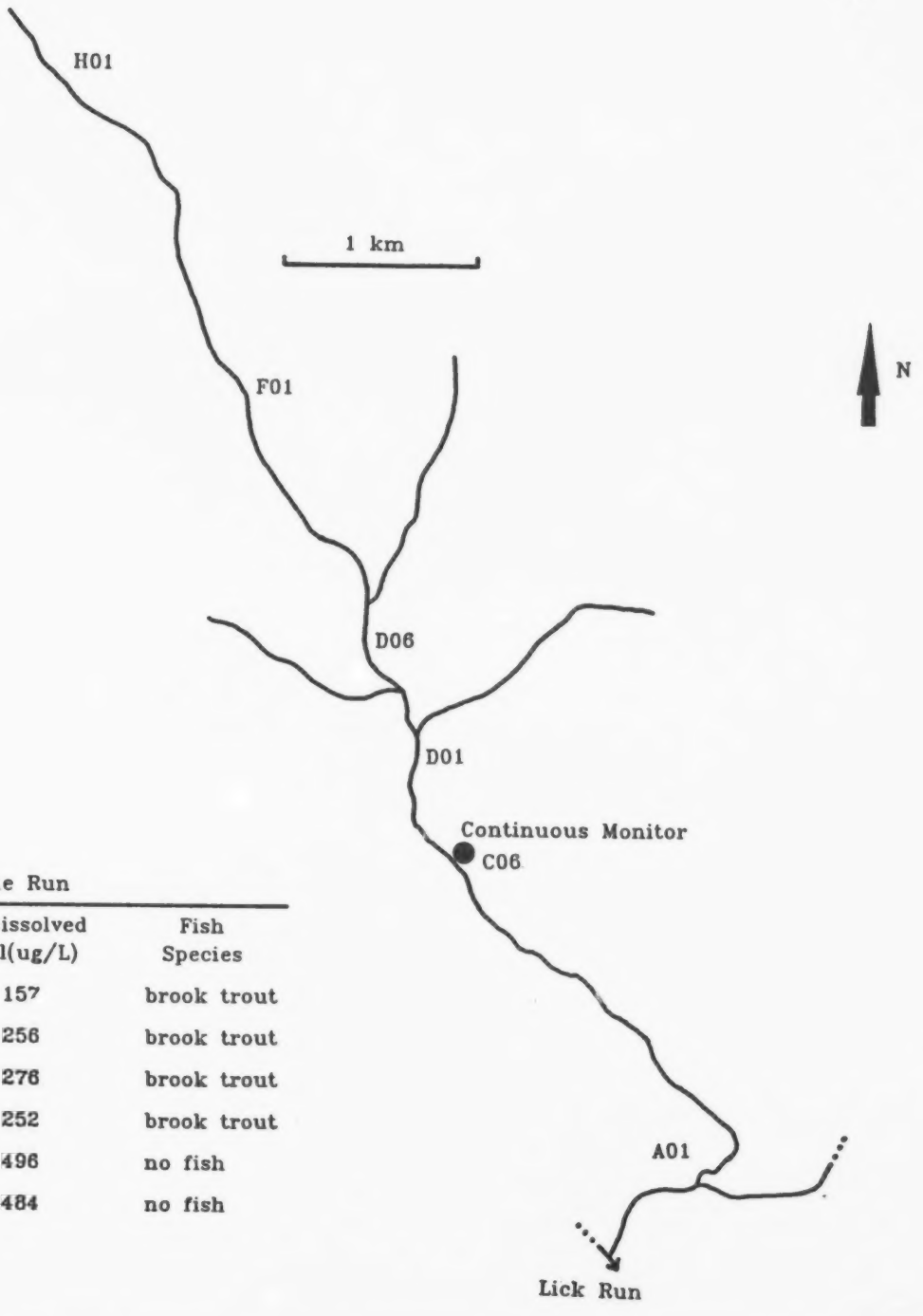
Two significant episodes of high aluminum concentration occurred on Linn Run (Figure 64) during the Spring bioassay period. Episodes of lesser magnitude occurred on the other study streams (Figures 65-68). These episodes were associated with substantial mortality of bioassay fish at the Linn, Stone and Roberts Run sites. Mortality on these three streams occurred during



Linn Run

Site	pH	Dissolved Al(ug/L)	Fish Species
D07	6.7	9	mottled sculpin brook trout
H09	6.5	18	brook trout mottled sculpin
I06	6.1	49	brook trout
K04	5.0	304	no fish
L07	4.7	535	no fish

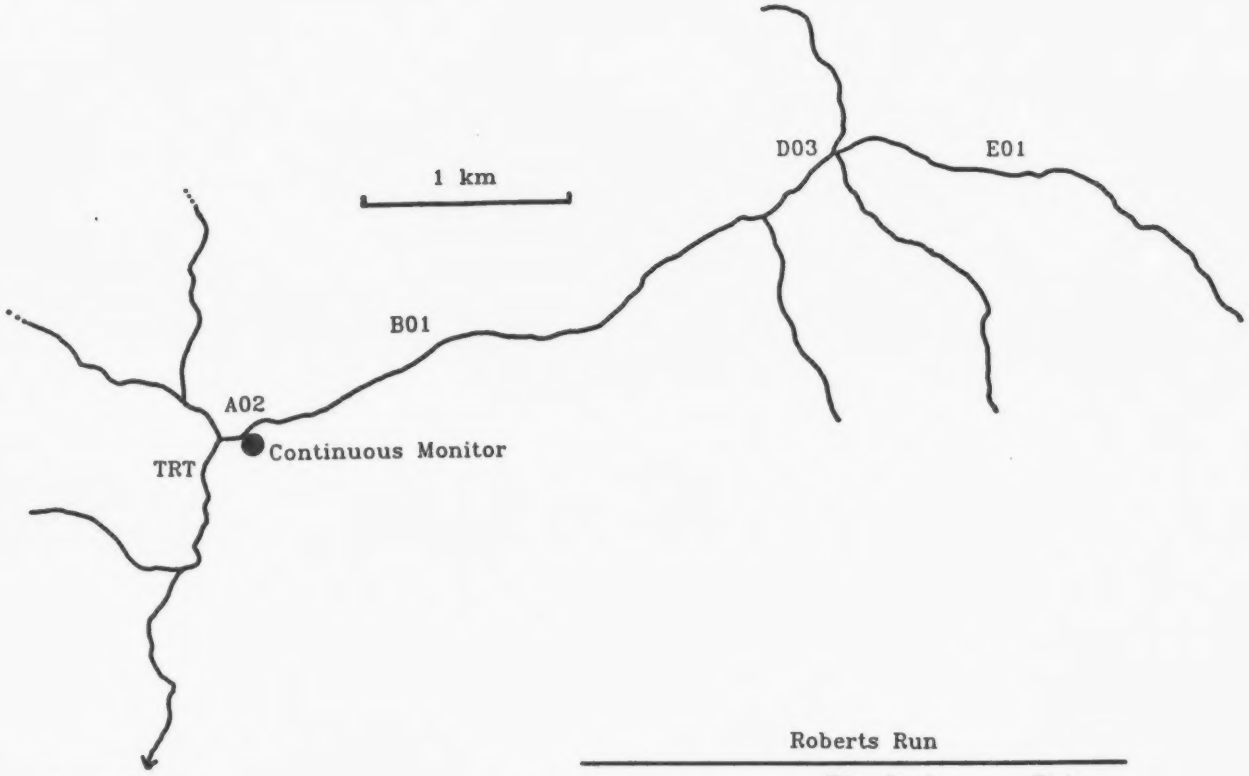
Figure 54. Linn Run drainage network showing fish communities and spatial variability in stream pH and dissolved aluminum concentration. All water samples were collected on May 23, 1989 while stream discharge at the continuous monitor was 0.033 $m^3/s/Km^2$.



Stone Run

Site	pH	Dissolved Al(ug/L)	Fish Species
A01	5.1	157	brook trout
C06	4.9	256	brook trout
D01	4.8	276	brook trout
D06	4.8	252	brook trout
F01	4.4	496	no fish
H01	4.3	484	no fish

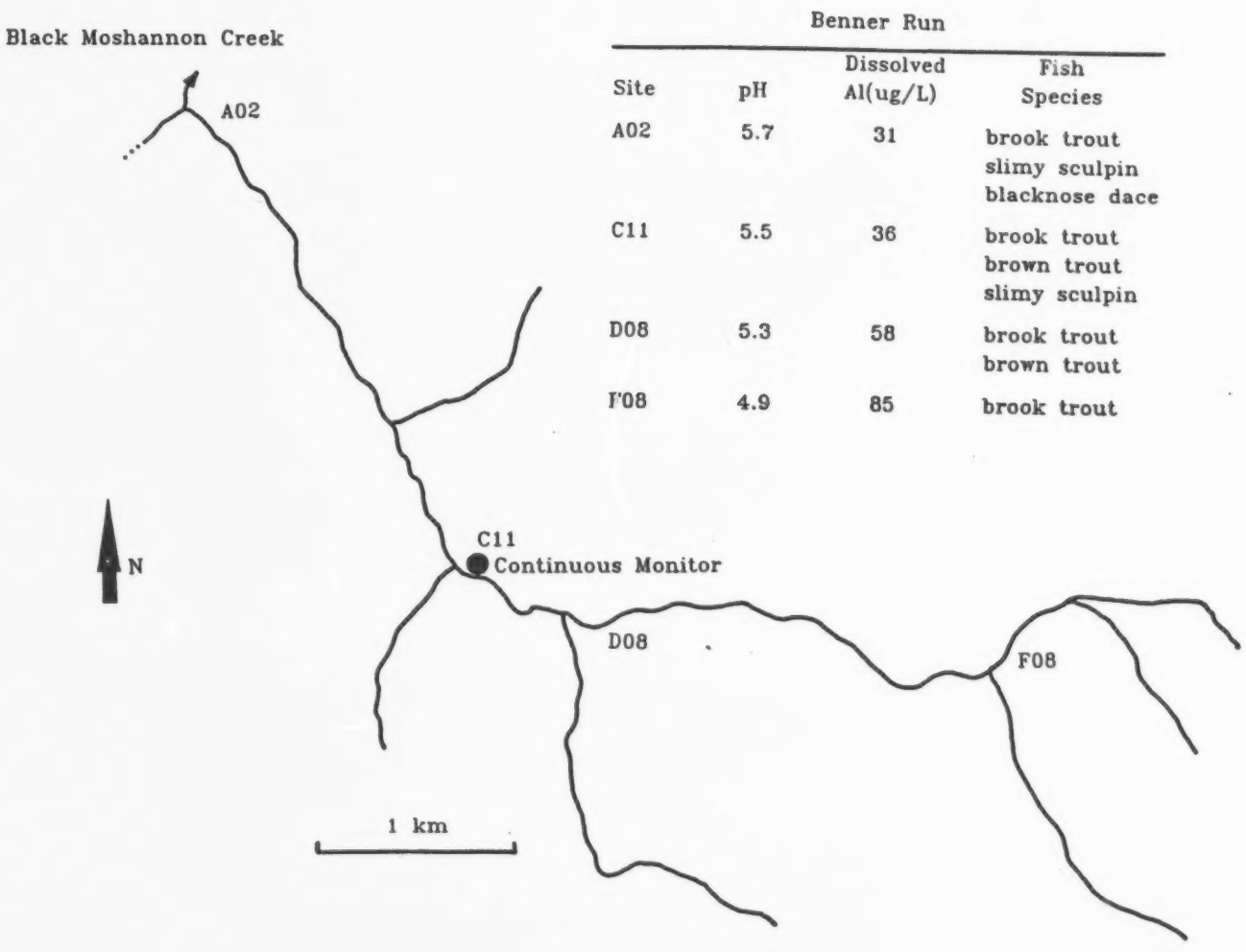
Figure 55. Stone Run drainage network showing fish communities and spatial variability in stream pH and dissolved aluminum concentration. All water samples were collected on May 18, 1989 while stream discharge at the continuous monitor was 0.063 $m^3/s/Km^2$.



Roberts Run

Site	pH	Dissolved Al(ug/L)	Fish Species
TRT	4.7	129	brook trout
A02	4.8	116	brook trout
B01	4.7	128	brook trout
D03	4.5	130	brook trout
E01	4.5	119	no fish

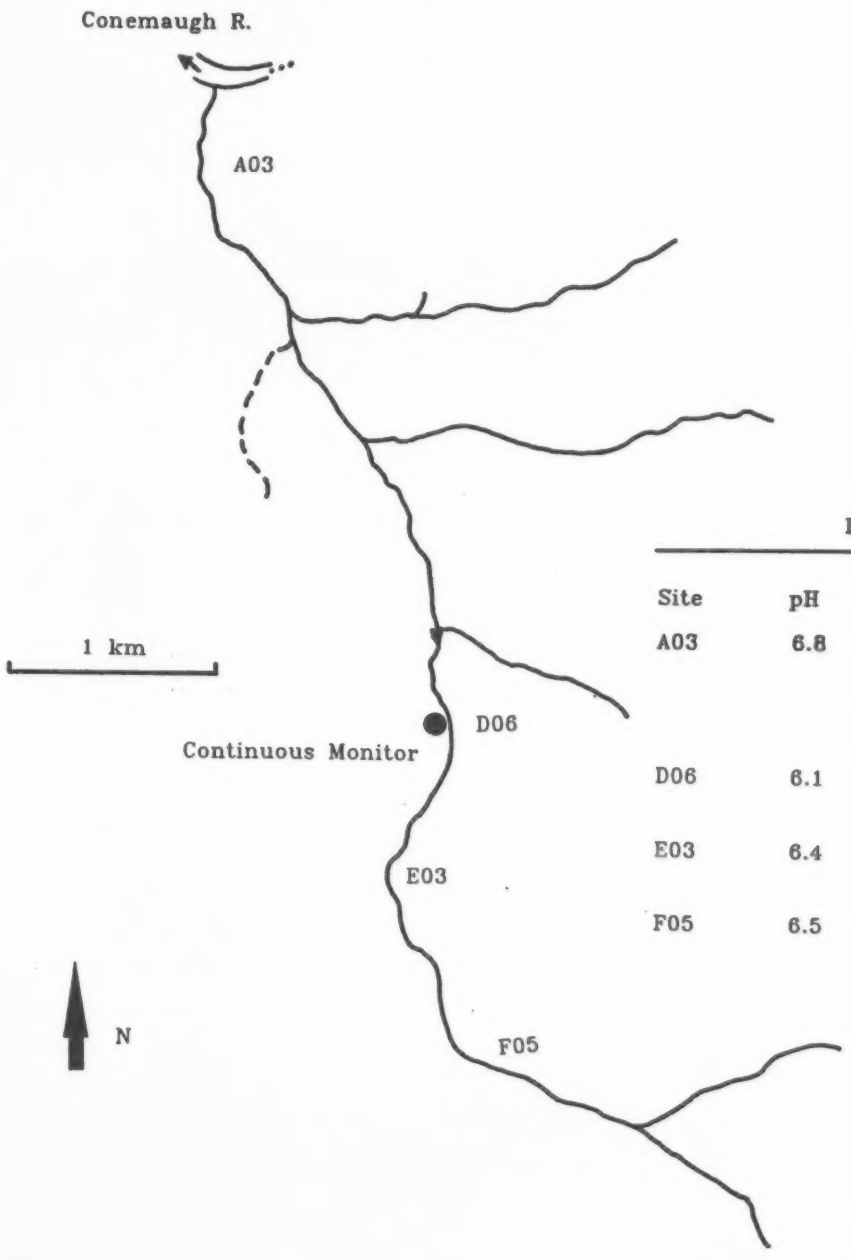
Figure 56. Roberts Run drainage network showing fish communities and spatial variability in stream pH and dissolved aluminum concentration. All water samples were collected on May 18, 1989 while stream discharge at the continuous monitor was 0.072 $m^3/s/Km^2$.



Benner Run

Site	pH	Dissolved Al(ug/L)	Fish Species
A02	5.7	31	brook trout slimy sculpin blacknose dace
C11	5.5	36	brook trout brown trout slimy sculpin
D08	5.3	58	brook trout brown trout
F08	4.9	85	brook trout

Figure 57. Benner Run drainage network showing fish communities and spatial variability in stream pH and dissolved aluminum concentration. All water samples were collected on May 19, 1989 while stream discharge at the continuous monitor was 0.107 $m^3/s/Km^2$.



Baldwin Creek

Site	pH	Dissolved Al(ug/L)	Fish Species
A03	6.8	10	mottled sculpin blacknose dace white sucker creek chub
D06	6.1	19	brook trout mottled sculpin
E03	6.4	14	brook trout mottled sculpin
F05	6.5	4	brook trout

Figure 58. Baldwin Creek drainage network showing fish communities and spatial variability in stream pH and dissolved aluminum concentration. All water samples were collected on May 22, 1989 while discharge was 0.032 $m^3/s/Km^2$.

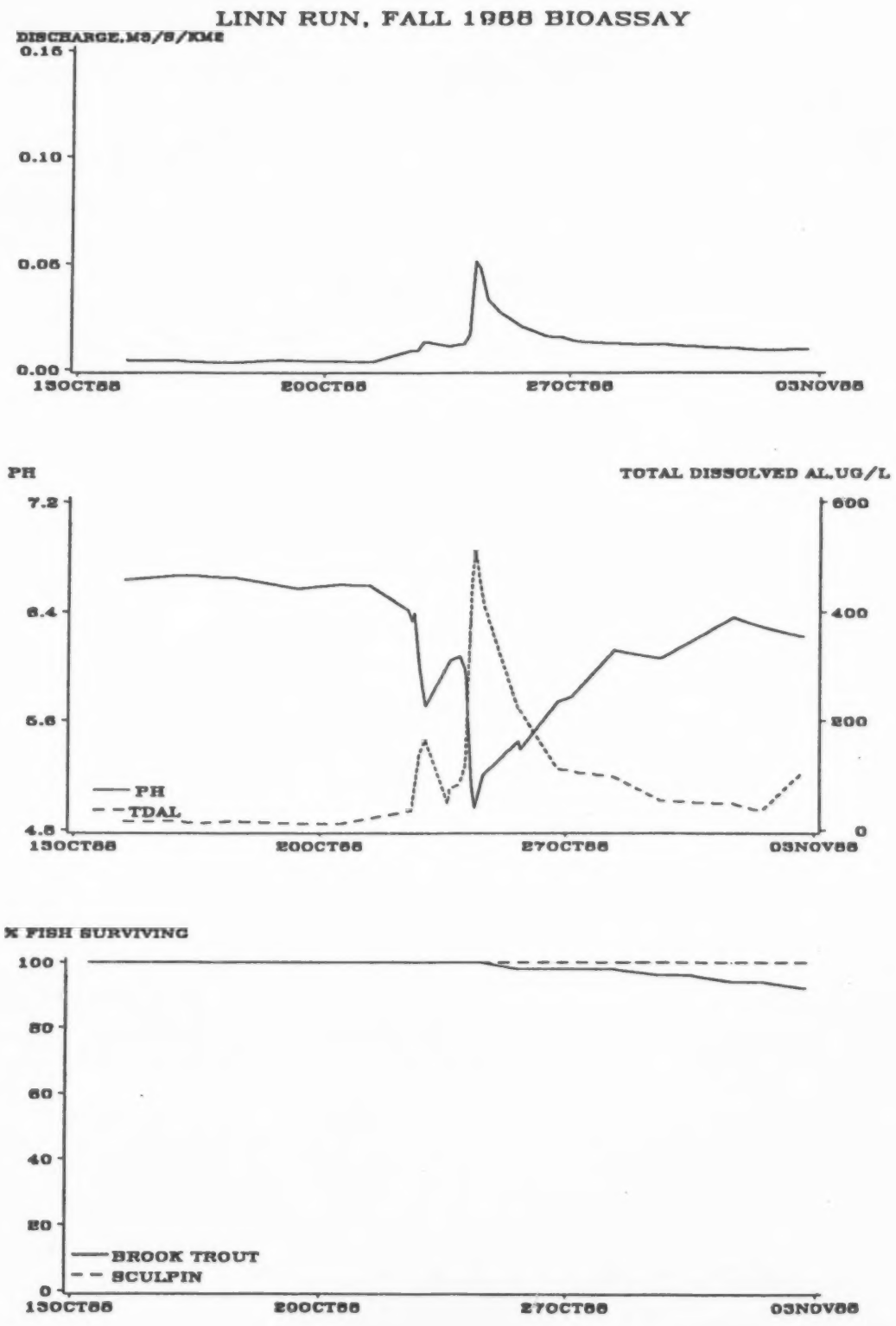


Figure 59. Flow, bioassay, pH and total dissolved aluminum data for Linn Run, Fall 1988 period.

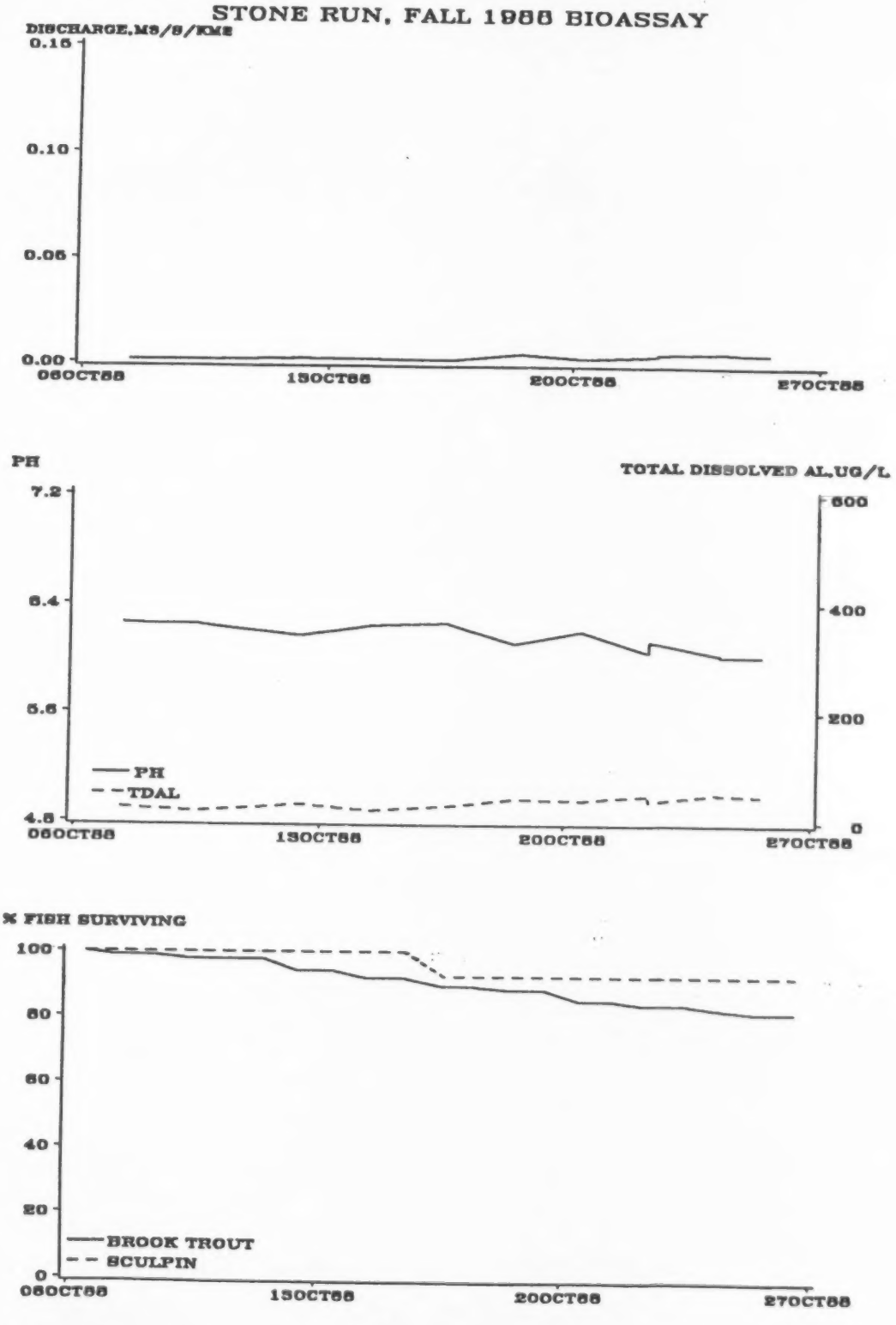


Figure 60. Flow, bioassay, pH and total dissolved aluminum data for Stone Run, Fall 1988 period.

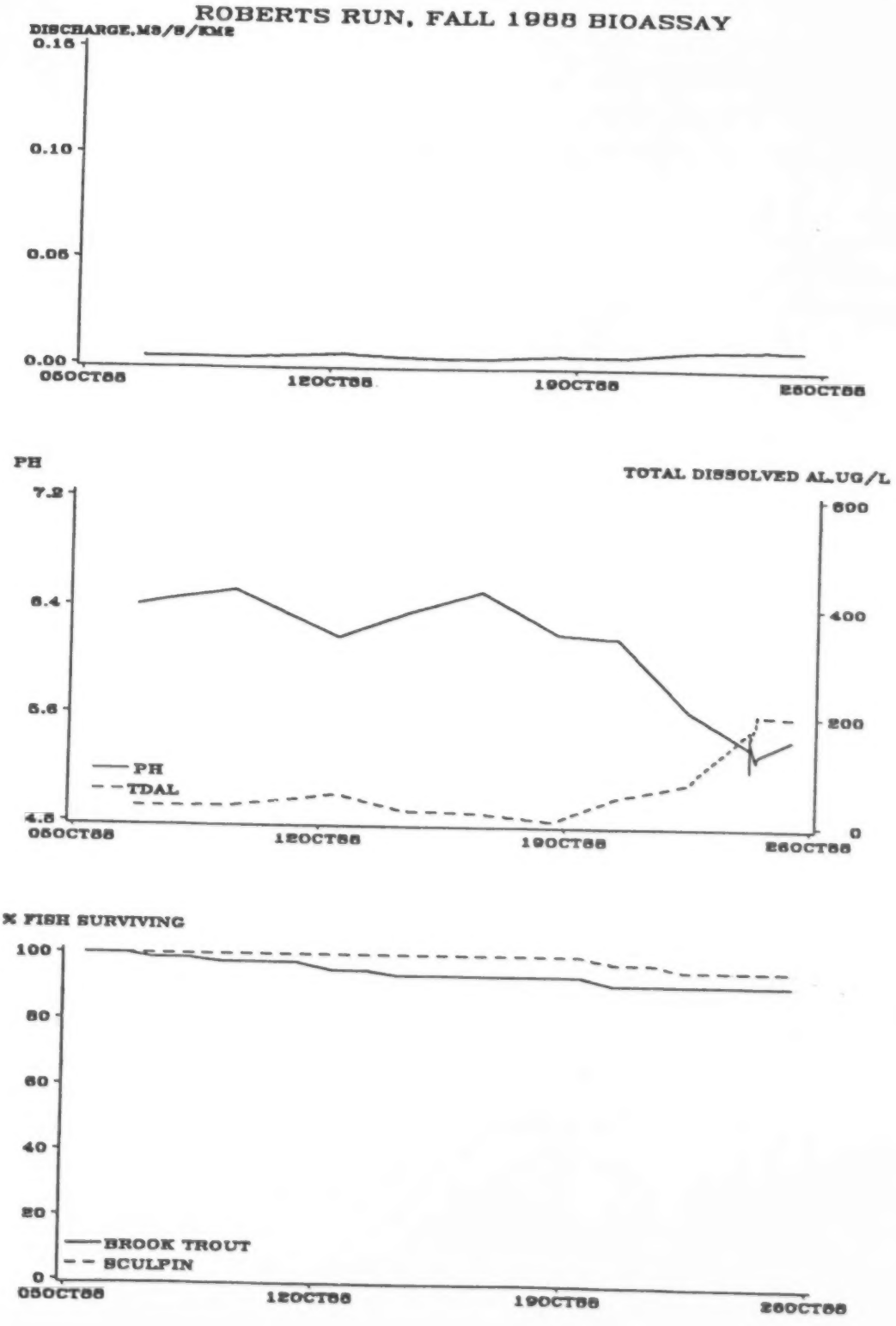


Figure 61. Flow, bioassay, pH and total dissolved aluminum data for Roberts Run, Fall 1988 period.

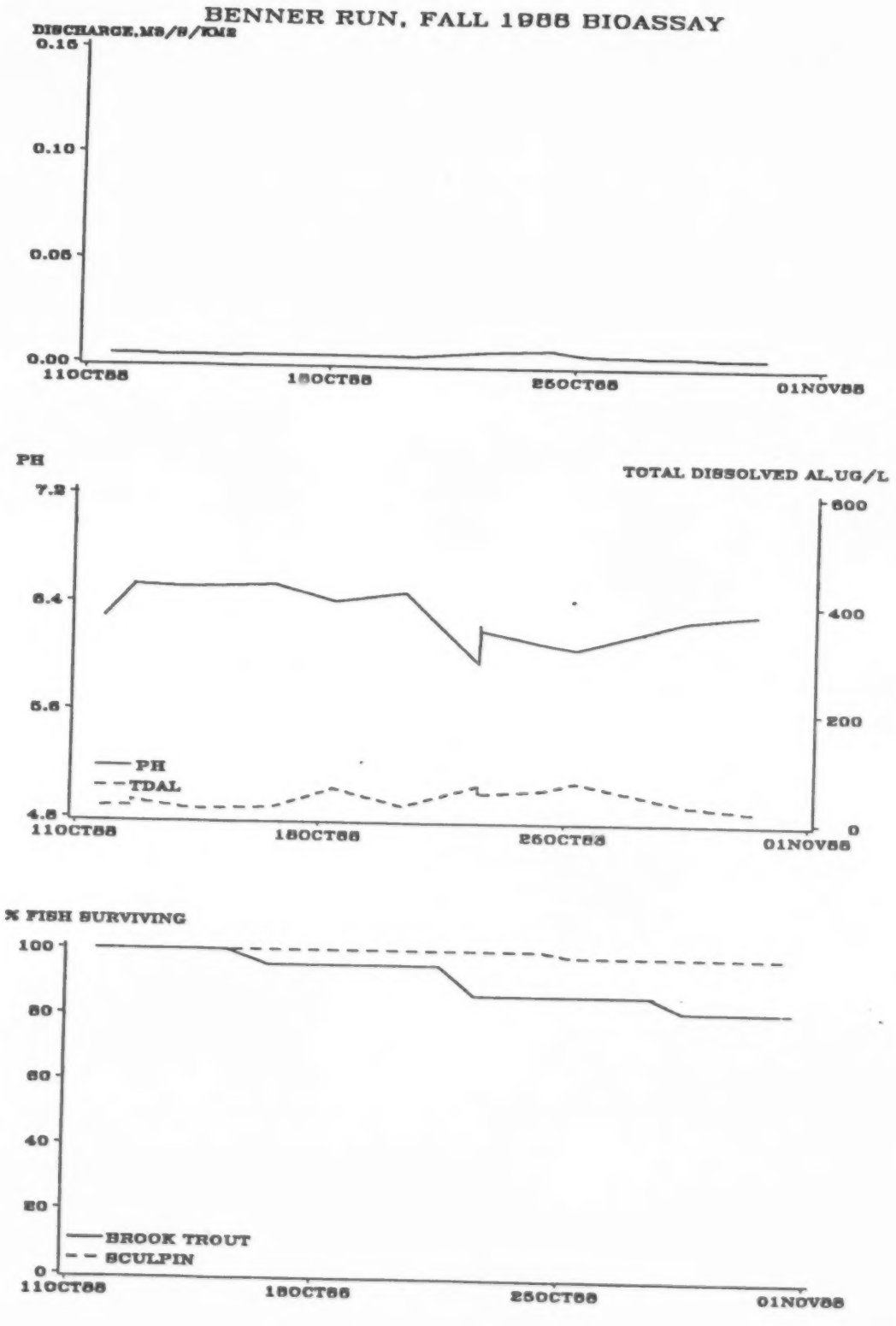


Figure 62. Flow, bioassay, pH and total dissolved aluminum data for Benner Run, Fall 1988 period.

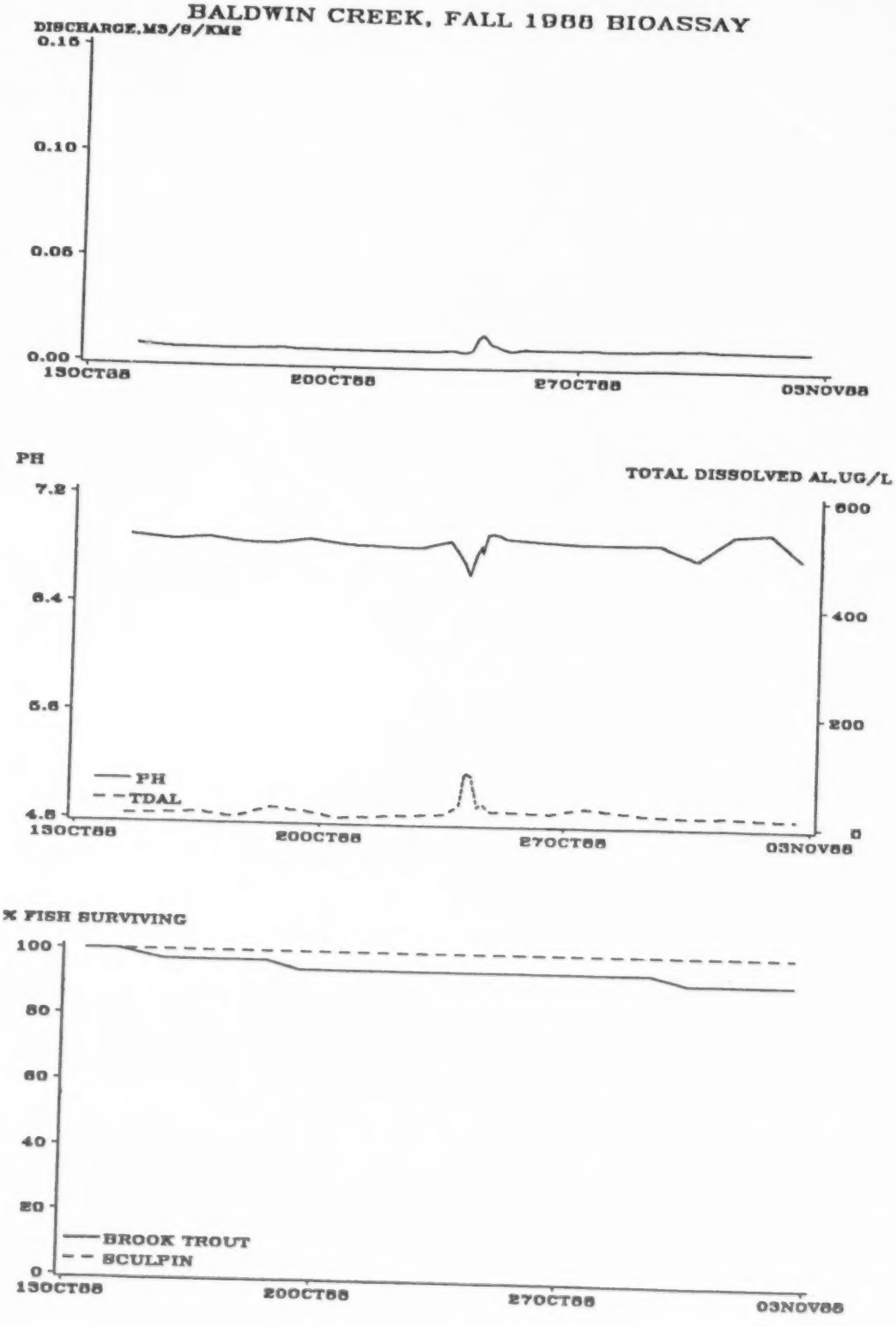


Figure 63. Flow, bioassay, pH and total dissolved aluminum data for Baldwin Creek, Fall 1988 period.

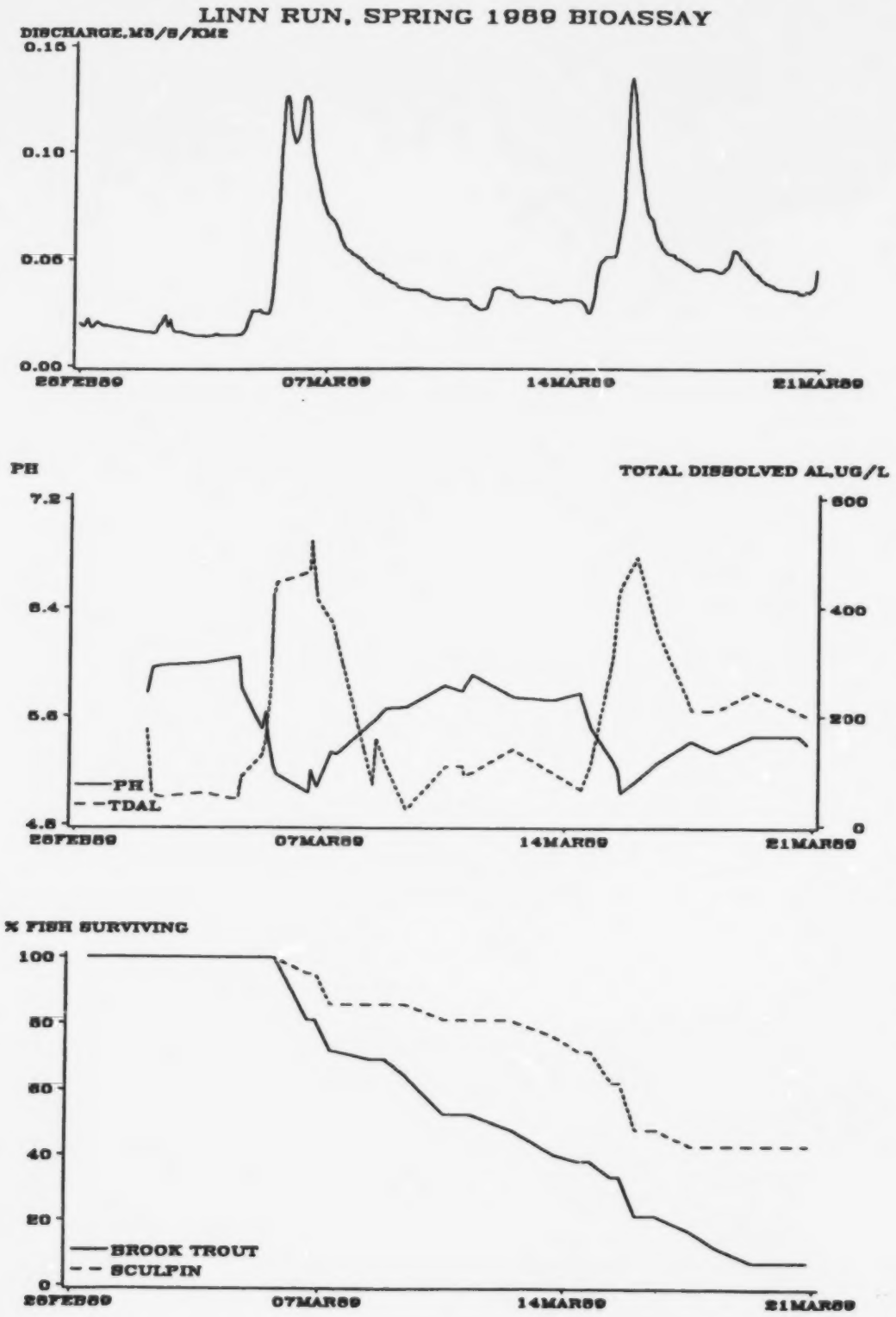


Figure 64. Flow, pH, total dissolved aluminum and fish survival for Spring 1989 bioassay on Linn Run.

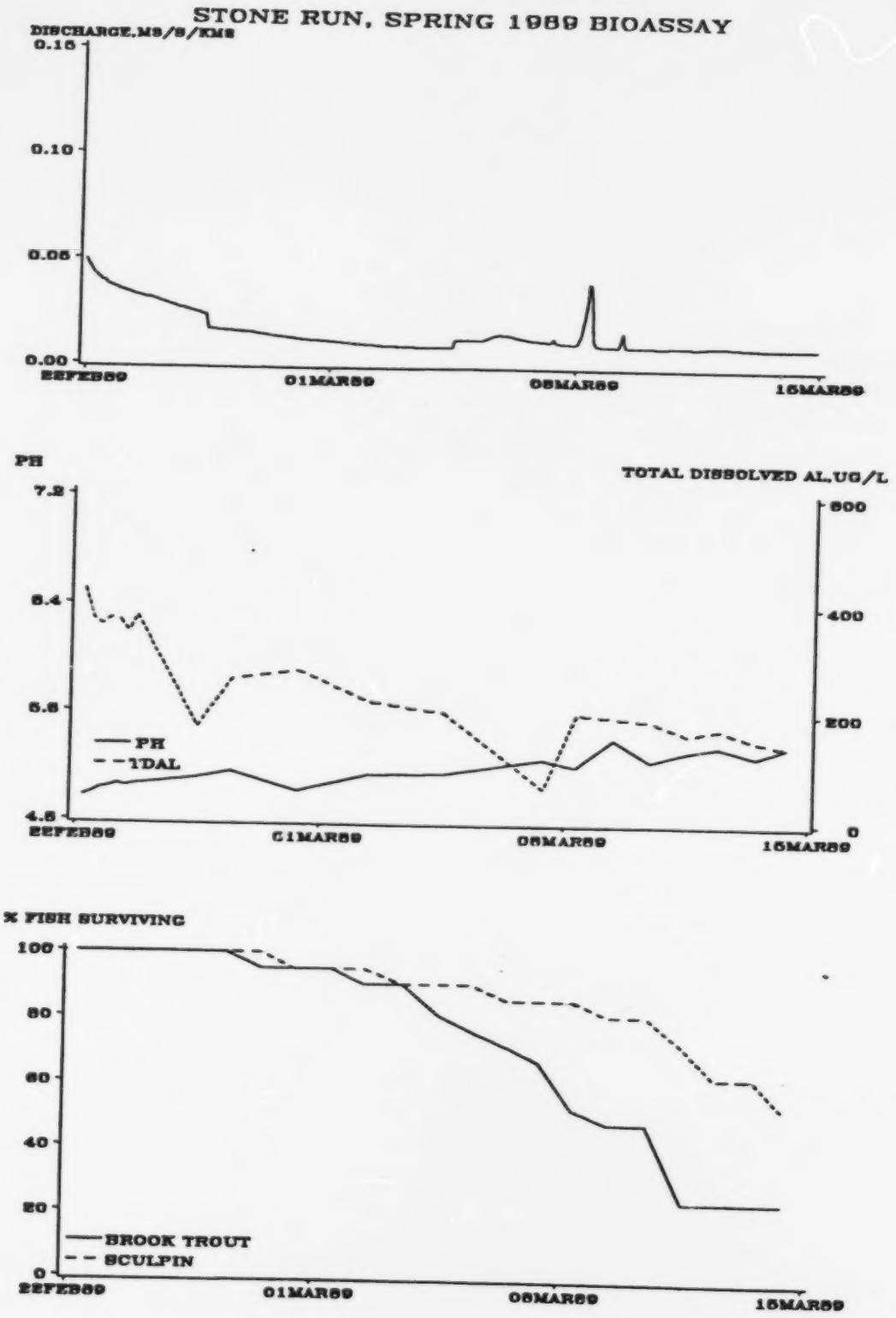


Figure 65. Flow, pH, total dissolved aluminum and fish survival for the Spring 1989 bioassay on Stone Run.

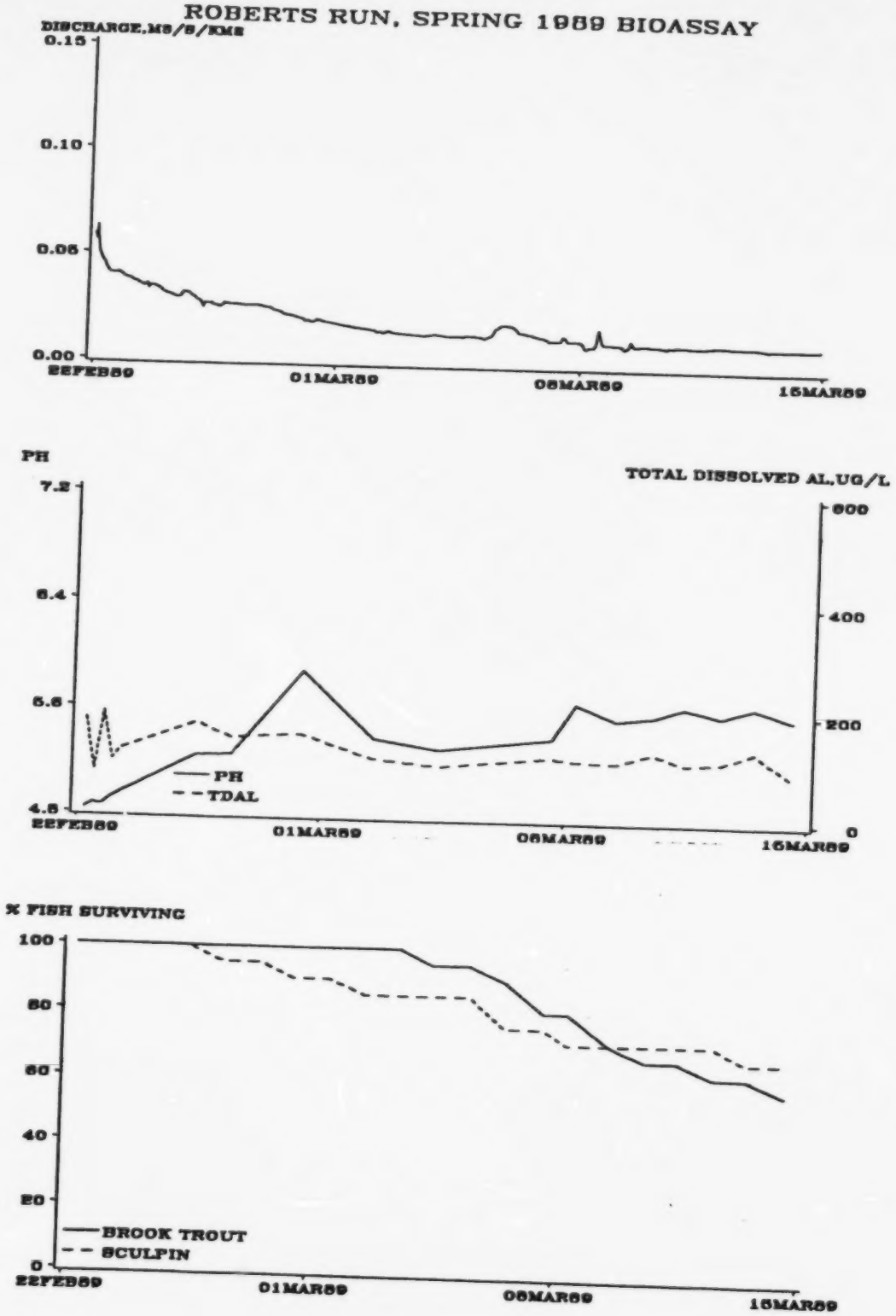


Figure 66. Flow, pH, total dissolved aluminum and fish survival for the Spring 1989 bioassay on Roberts Run.

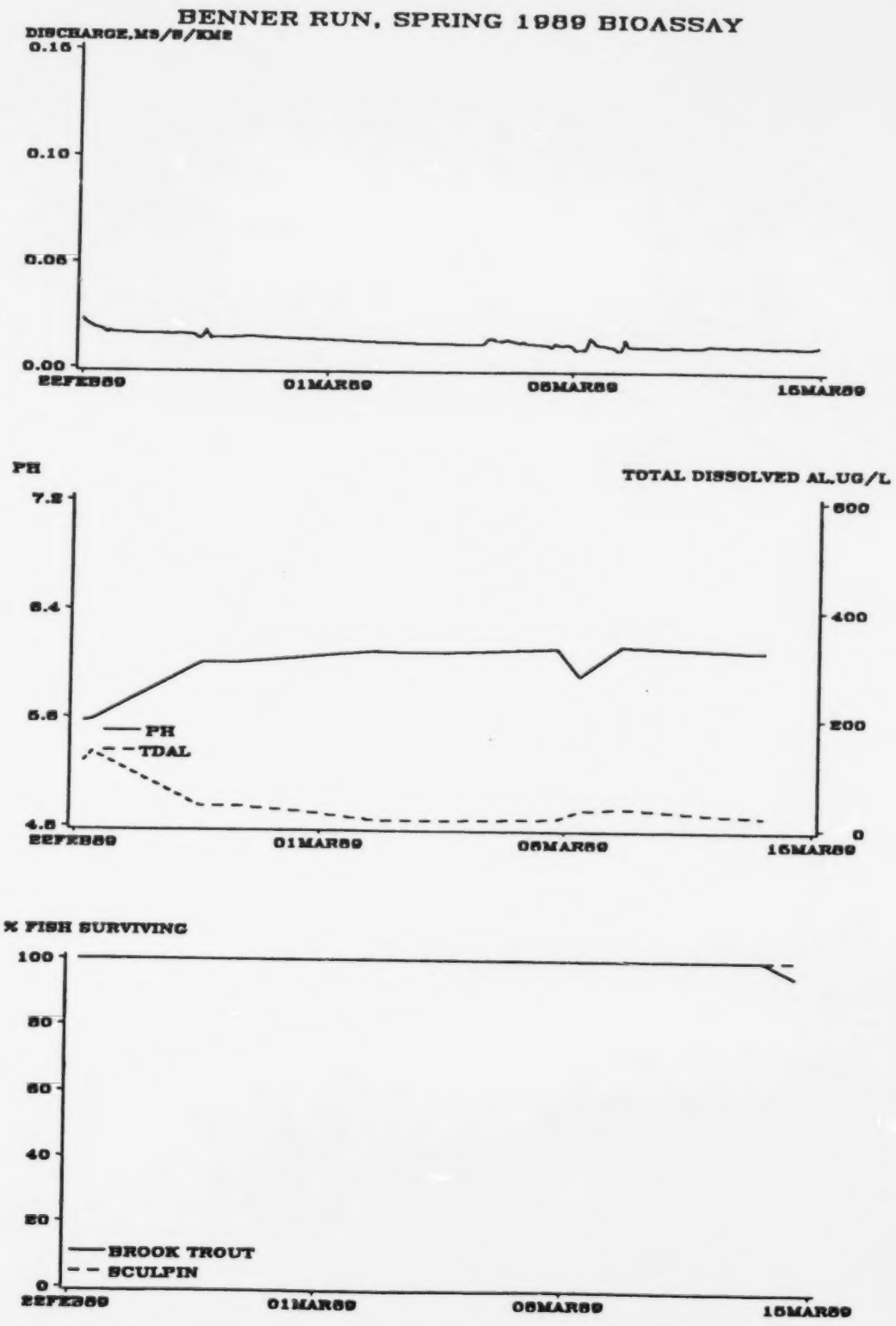


Figure 67. Flow, pH, total dissolved aluminum and fish survival for the Spring 1989 bioassay on Benner Run.

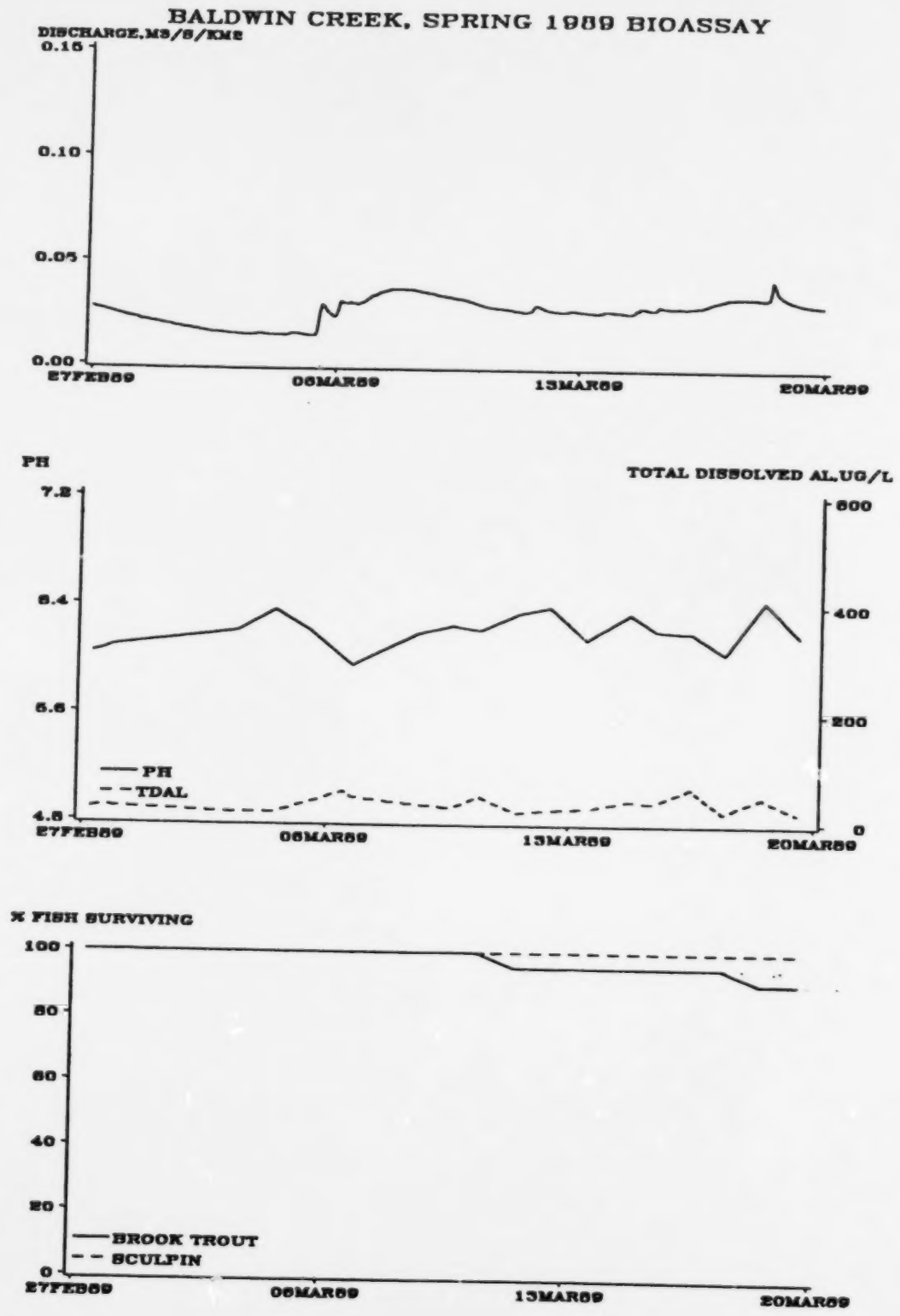


Figure 68. Flow, pH, total dissolved aluminum and fish survival for the Spring 1989 bioassay on Baldwin Creek.

protracted periods of high total dissolved aluminum concentrations (near or above 200 µg/l). There was no significant mortality on Baldwin Creek or Benner Run and total dissolved aluminum concentration remained well below 200 µg/l on these streams.

Average daily mortality for the 20 day Fall 1988 and Spring 1989 bioassay periods was positively correlated with maximum aluminum concentration (Figure 69) and inversely correlated with minimum pH (Figure 70) for sculpins and brook trout. However, data from Linn Run, Fall 1988 do not fit well because episodes had similar peak chemistry as episodes in Spring, but few fish died during the short duration of the Fall episodes. Average daily mortality showed stronger relationships to median aluminum (Figure 71) and pH (Figure 72) for both brook trout and sculpin. Spring 1989 daily mortality was elevated for both sculpins and brook trout when 20-day median dissolved aluminum values exceeded 100 µg/l and median pH values were less than 5.5.

Minimum pH's near 5.0 resulted in high mortality, but as has been indicated in previous studies with respect to brook trout, this is probably largely the result of concomitantly high total dissolved aluminum concentrations. Due to the physiological mechanism of acid/aluminum toxicity, the duration of low pH and high aluminum must persist for several days to cause significant mortality. Sculpins appeared to be at least as tolerant as brook trout to the episodes monitored.

Telemetry Experiments

Radio-tracking experiments were conducted in Linn Run and Baldwin Creek to determine if brook trout movement was related to severity of acid episodes. Fish locations were recorded daily and water samples were collected daily at each fish location to determine whether pH and total dissolved aluminum levels at fish locations differed from stream chemistry measured at the continuous monitoring site of each stream. When fish moved more than 25 m from one day to the next, a sample was collected at both their current and previous location to determine whether movement resulted in exposure to increased ambient pH and reduced ambient aluminum concentration.

We found limited net movement prior to acid runoff episodes on both streams (Figures 73 and 74). Acid runoff episodes led to much greater movement on the more acidic Linn Run, compared to Baldwin Creek during both Fall 1988 and Spring 1989 field seasons (Figures 73 and 74). Downstream movement in Linn Run during fall occurred even though episode duration was not long enough to result in mortality of caged fish. One third of the 15 fish released in Linn Run during Spring 1989 were found dead (Figure 75). We did not find any dead fish in Baldwin Creek during fall or spring. Furthermore, we did not find any dead fish in Linn Run during fall.

In general, ambient pH was higher and aluminum concentration was lower at individual fish locations than at the continuous monitor site at Linn Run. During a series of successive episodes, brook trout in Linn Run moved downstream several hundred meters and were found in water with higher pH and lower dissolved aluminum concentration compared to chemistry at the continuous monitor or chemistry at their previous locations. Stream water in the study section of Linn Run was mixed with alkaline groundwater from seeps, springs, and spring fed tributaries and thus provided refuges for moving trout. For

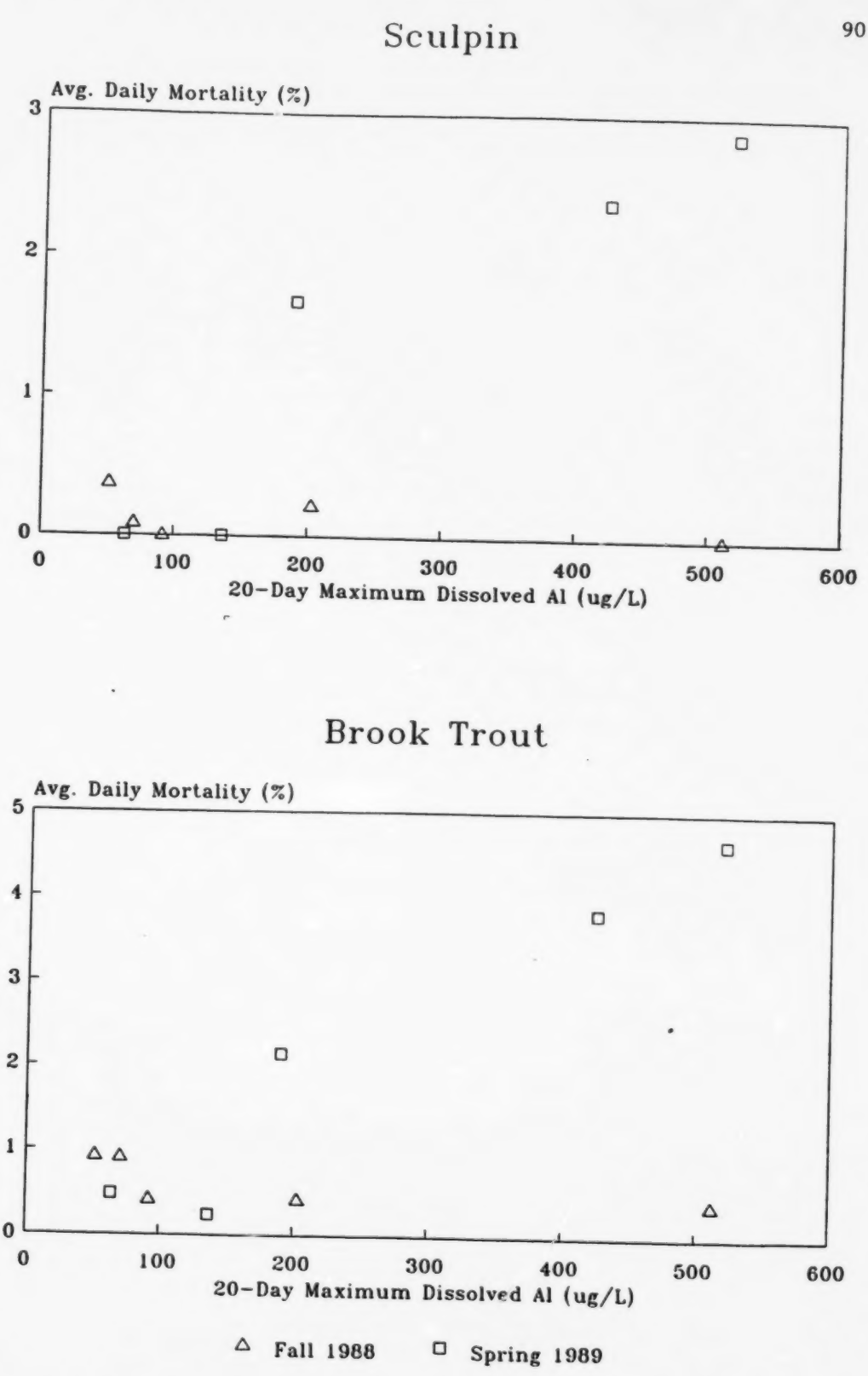
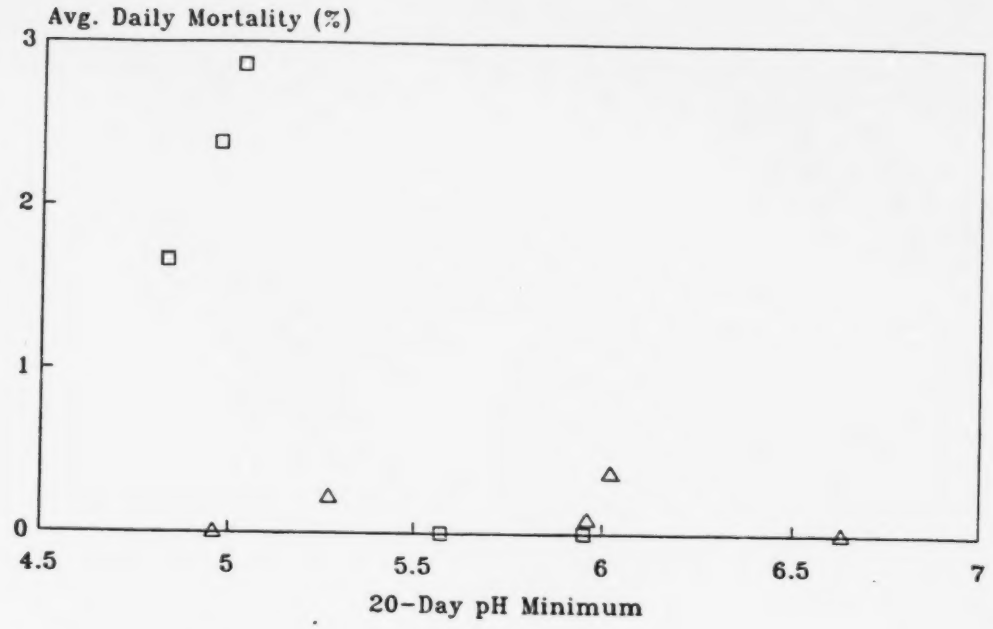


Figure 69. Fish mortality in relation to maximum aluminum concentrations for the Fall 1988 and Spring 1989 bioassay periods.

Sculpin



Brook Trout

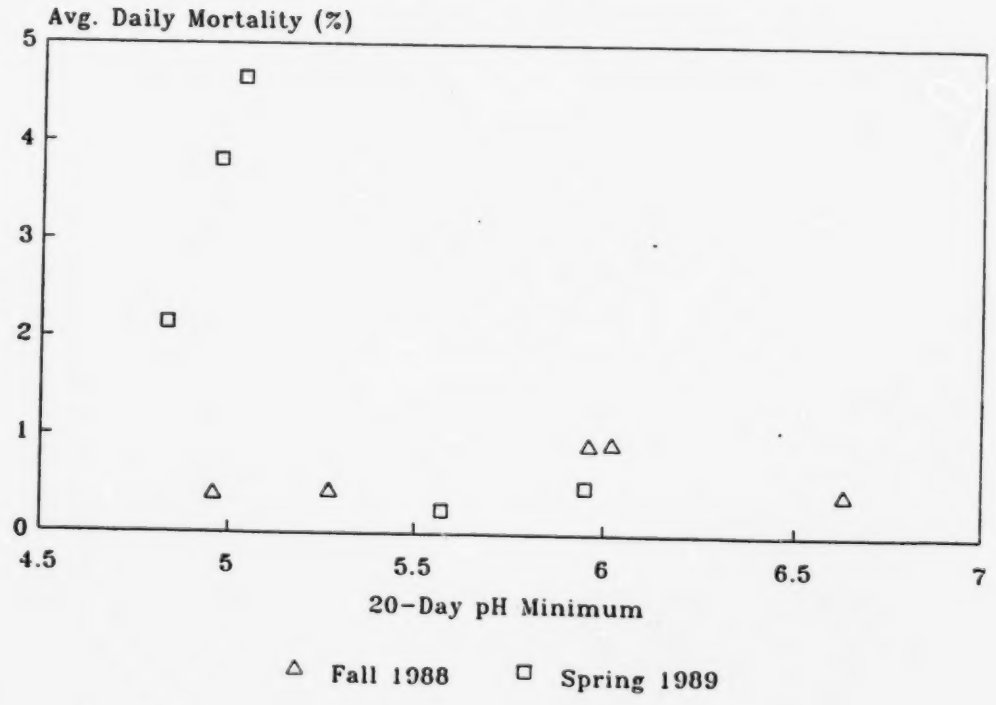
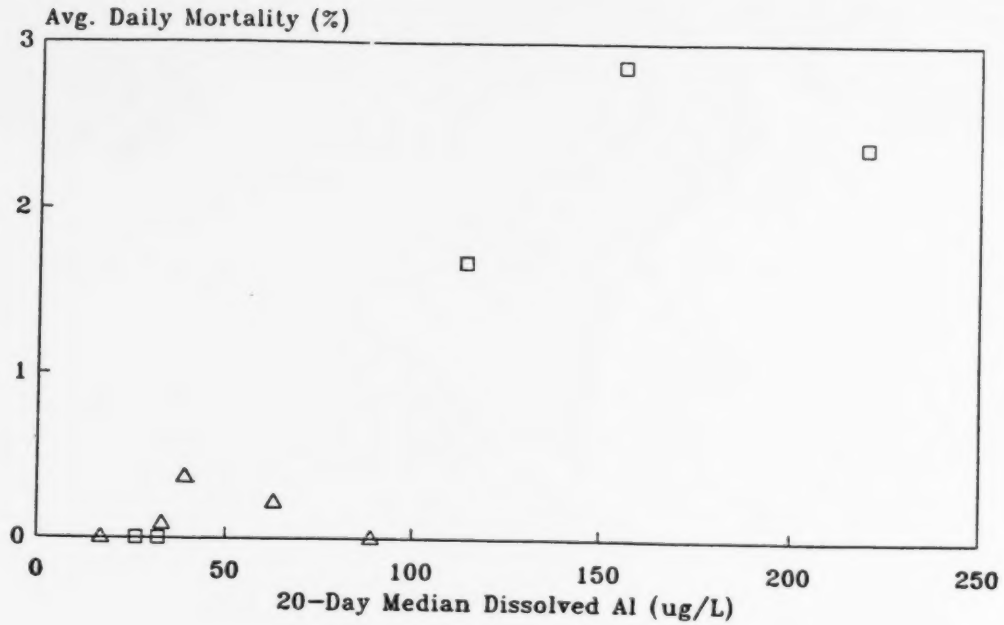


Figure 70. Fish mortality in relation to minimum pH for Fall 1988 and Spring 1989 bioassay periods.

Sculpin



Brook Trout

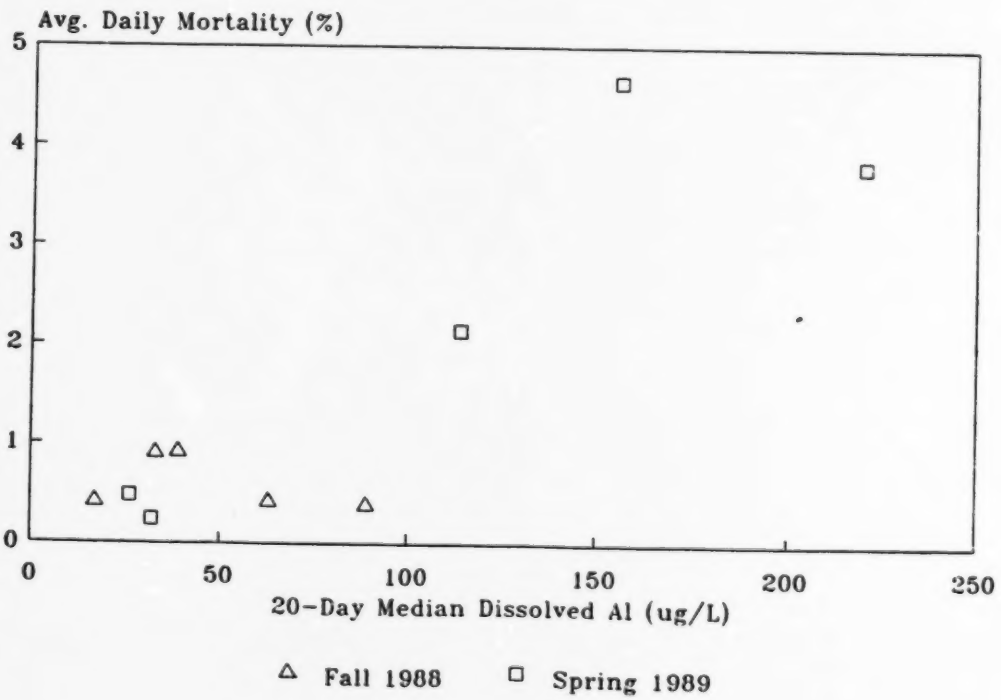


Figure 71. Fish mortality in relation to median total dissolved aluminum for Fall 1988 and Spring 1989 bioassay periods.

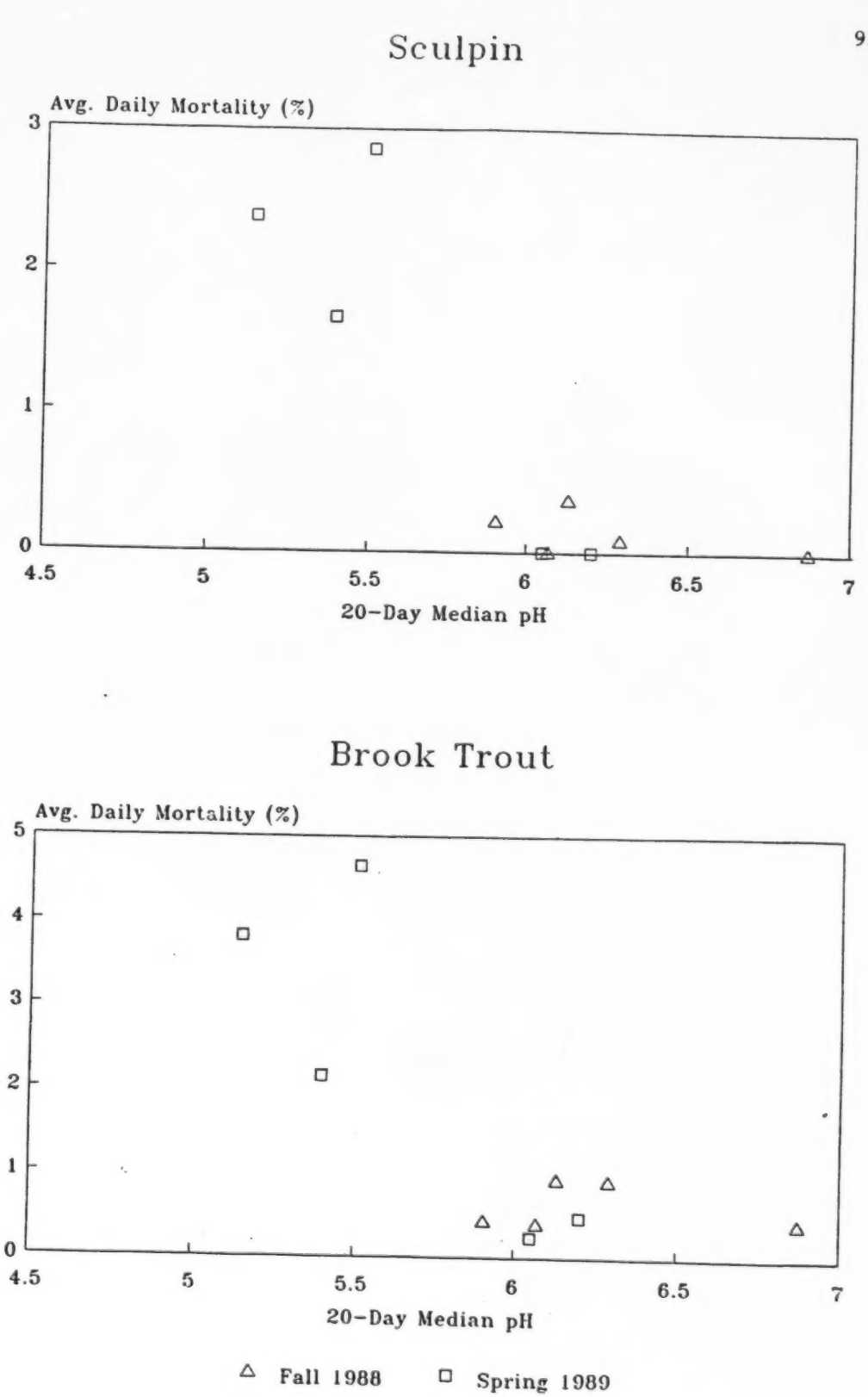


Figure 72. Fish mortality in relation to median pH for Fall 1988 and Spring 1989 bioassay periods.

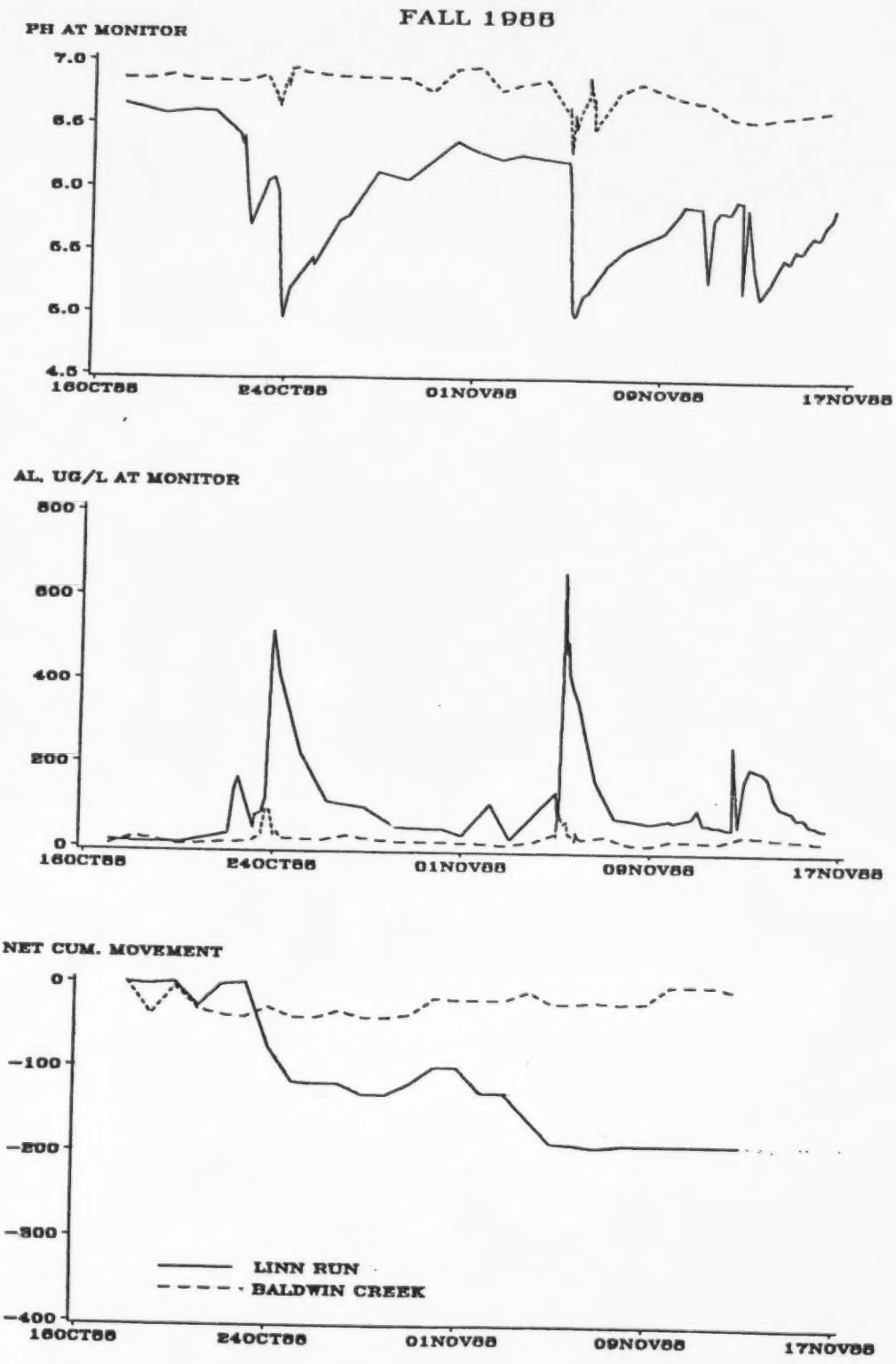


Figure 73. Linn Run and Baldwin Creek compared during the Fall 1988 telemetry period with respect to pH and total dissolved aluminum concentration from samples collected at the monitor and median net movement of brook trout relative to initial locations. Negative movement indicates downstream and medians are based on 3 to 7 fish.

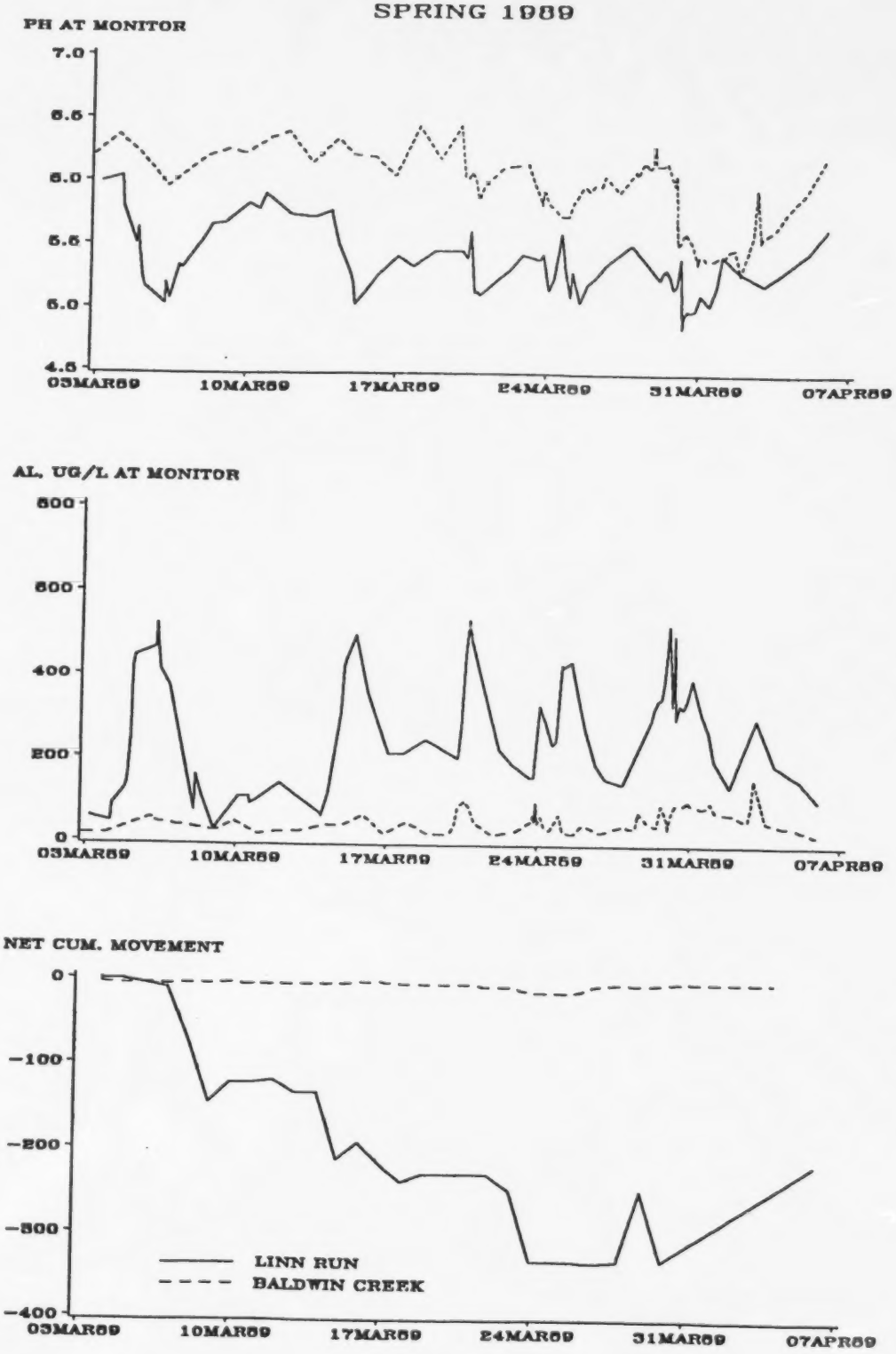


Figure 74. Linn Run and Baldwin Creek compared during the Spring 1989 telemetry period with respect to pH and total dissolved aluminum concentration from samples collected at the monitor and median net movement of brook trout relative to initial locations. Negative movement indicates downstream and medians are based on 3 to 15 fish.

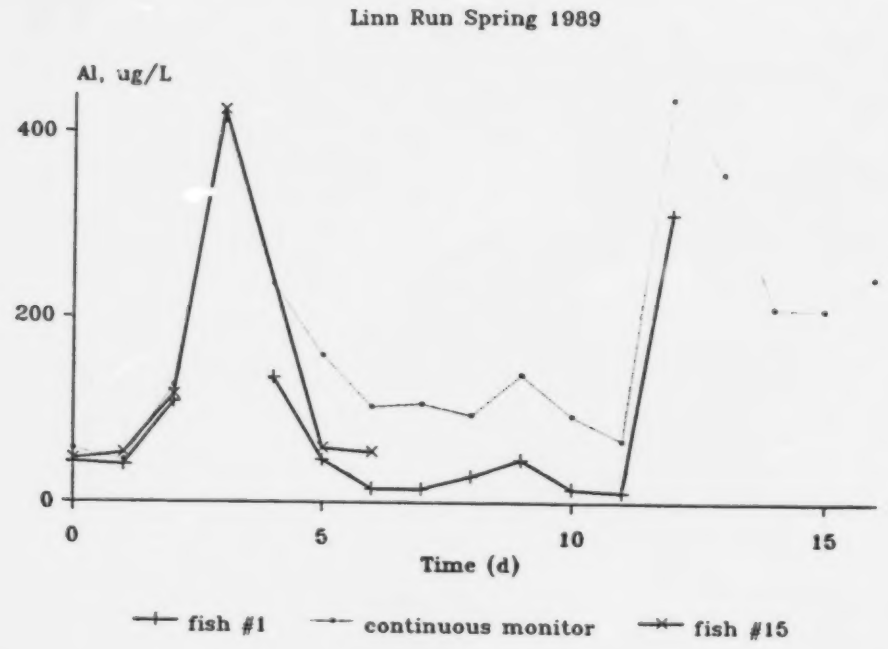


Figure 75. Linn Run pH and dissolved aluminum concentration for samples collected at the continuous monitor versus samples collected at locations of two telemetry fish that died. The last plotted pH value indicates when the fish were found dead.

example, fish number 7 moved downstream only 70m to a mircohabitat or refuge where acid episodes were less severe (Figure 76). By the fifth day of the spring telemetry study, fish number 23 had entered an alkaline, spring-fed tributary over 500m downstream of the continuous monitoring site on Linn Run. These fish were not exposed to the second episode measured at the continuous monitor. However, the availability of refuges is highly variable among and within stream systems. Certain headwater areas of many streams apparently have no alkaline groundwater input to serve as refuges.

Transplant Experiments

In early October 1988, prior to transplant operations, all streams supported relatively large populations of brook trout, except Linn Run (see Table 5). Age-0 trout were the most abundant age group. Low densities in Linn Run were due in part to the scarcity of age-0 trout.

Immediately after the October census, populations in each study section were adjusted to 75/0.1 ha. About one week later we resurveyed Benner, Roberts and Stone Runs to determine if marked trout were still present. We found that at least one-half of the transplanted trout were present, but more importantly, we found a significant recruitment of age-0 and adult trout (see Figure 77). One month after the transplants, about 50% of the marked fish remained in all streams, but total densities exceeded 75/0.1 ha due to recruitment of unmarked trout. The recruitment response was least evident in Linn Run, where adjacent trout population densities were lowest.

Throughout the winter the general pattern was a low rate of loss of marked fish and an increase in unmarked fish such that the total population remained fairly stable (Figures 77 and 78).

In February 1989 populations in all streams were reset at 75/0.1 ha. During the next 3 months, numbers of marked fish generally decreased while numbers of unmarked fish increased. Thus, population behavior was similar in fall (few toxic episodes) and spring (several toxic episodes).

We cannot distinguish between emigration and mortality with respect to the loss of marked fish. To quantify this loss, we computed instantaneous mortality rates per 30 days, so that spring and fall data could be compared. There was a positive, though variable, relation between instantaneous loss rates (Z/30 d) and numbers of unmarked fish (recruits) immigrating into study sections at least in Fall 1988 (Figure 79). Thus, Linn Run, which supports the smallest population of brook trout may have had the lowest loss rate of marked fish due to this factor, despite the most severe episodes.

Another way to view population behavior is to consider total density of all trout - both transplanted and immigrants. Mean densities of all brook trout were:

Benner	111
Stone	110
Baldwin	85
Roberts	76
Linn	42/0.1 ha.

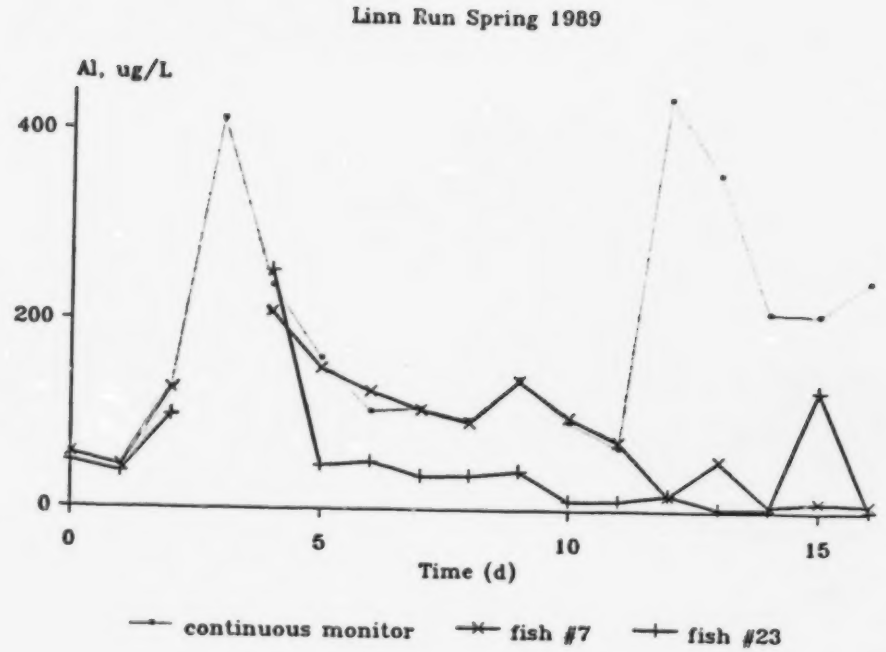
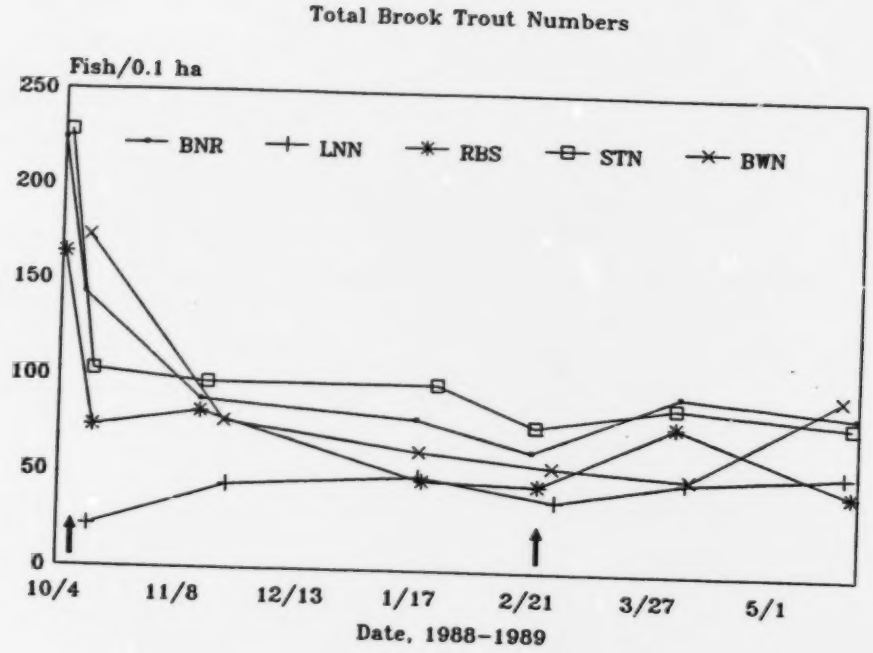


Figure 76. Linn Run pH and total dissolved aluminum concentration for samples collected at the continuous monitor versus samples collected at locations of two fish that moved to microhabitats or refuges of higher pH and lower dissolved aluminum.



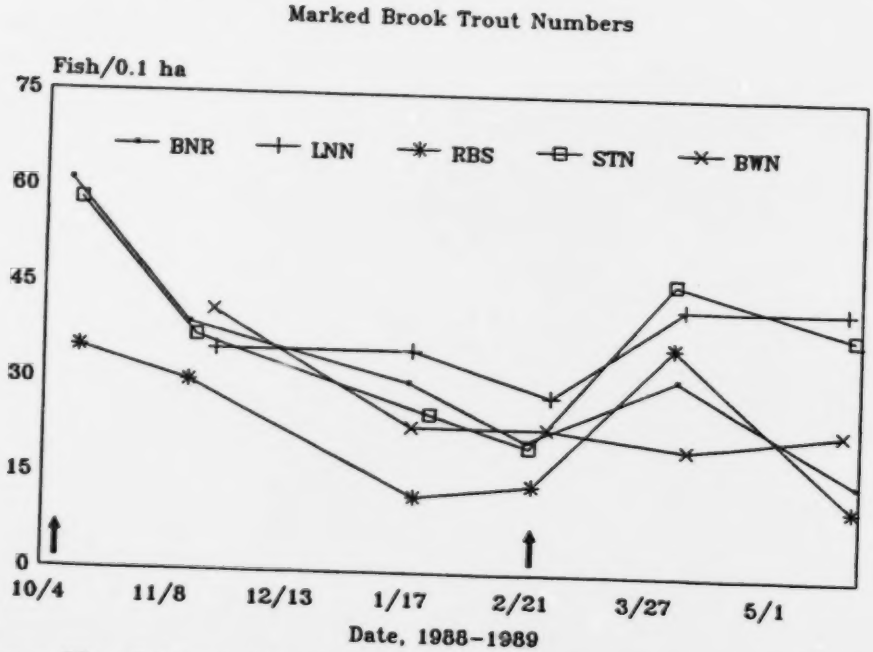
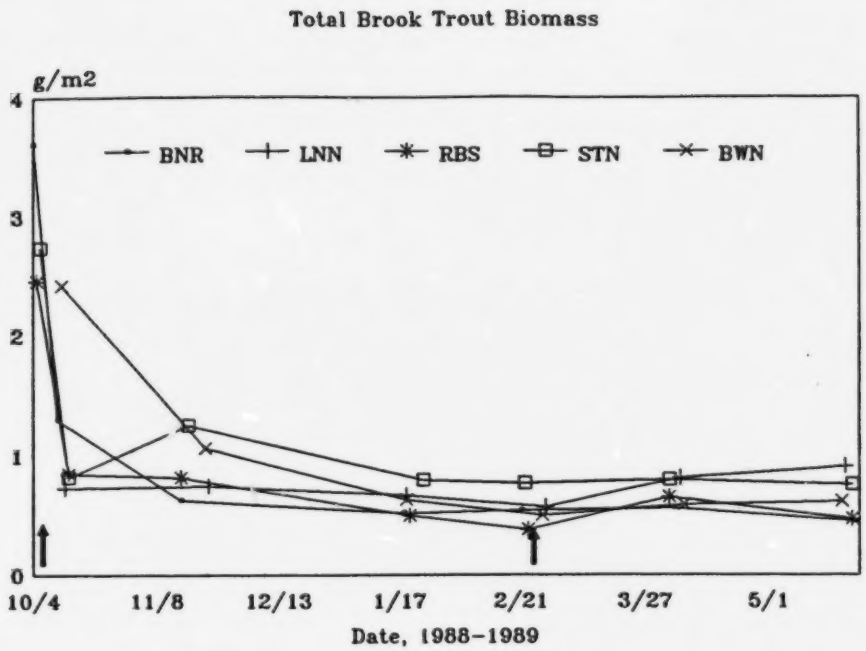


Figure 77. Estimated number of brook trout present in transplant sites. Arrows indicate approximate dates when the density of marked fish was set at 75/0.1 ha.



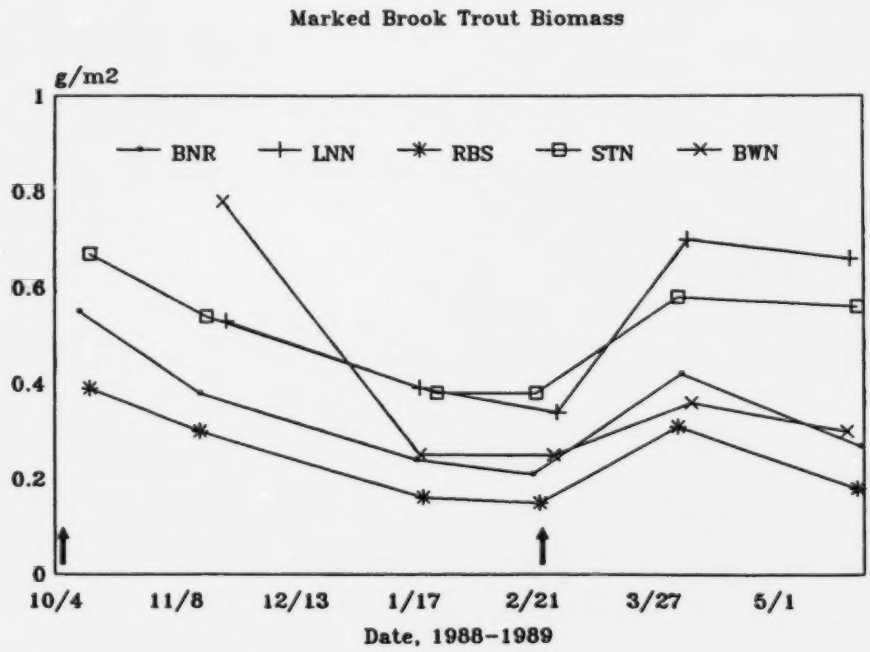
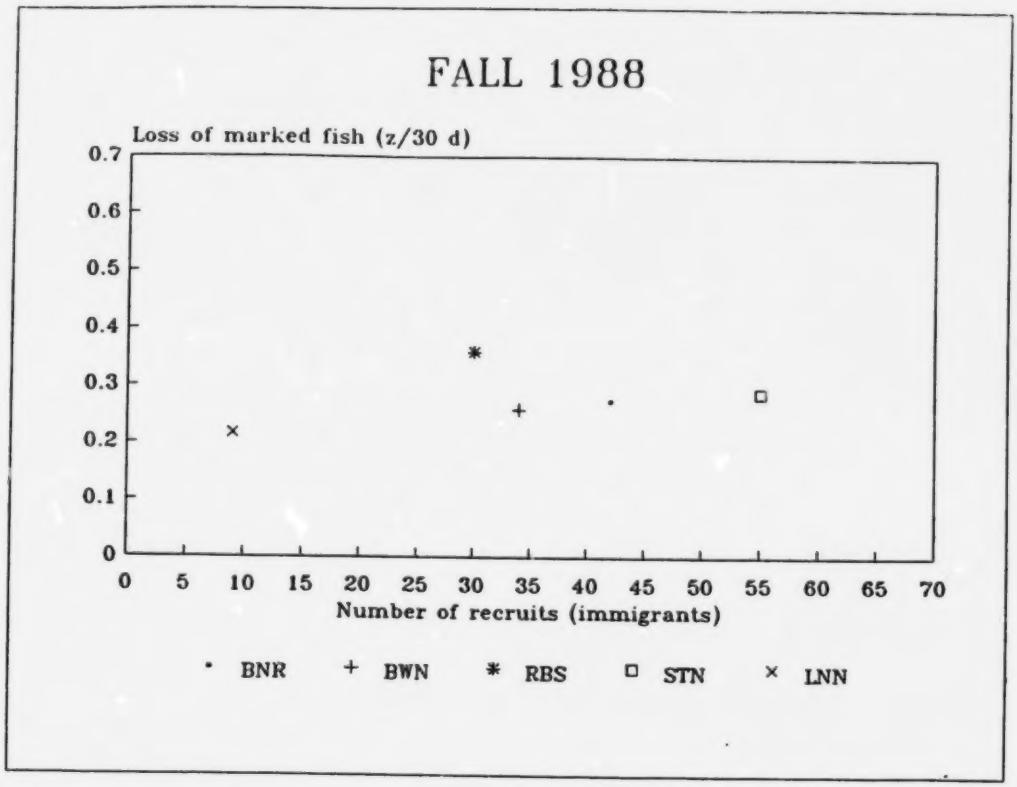


Figure 78. Estimated biomass of brook trout present in transplant sites. Arrows indicate approximate dates when the density of marked fish was set at 75/0.1 ha.



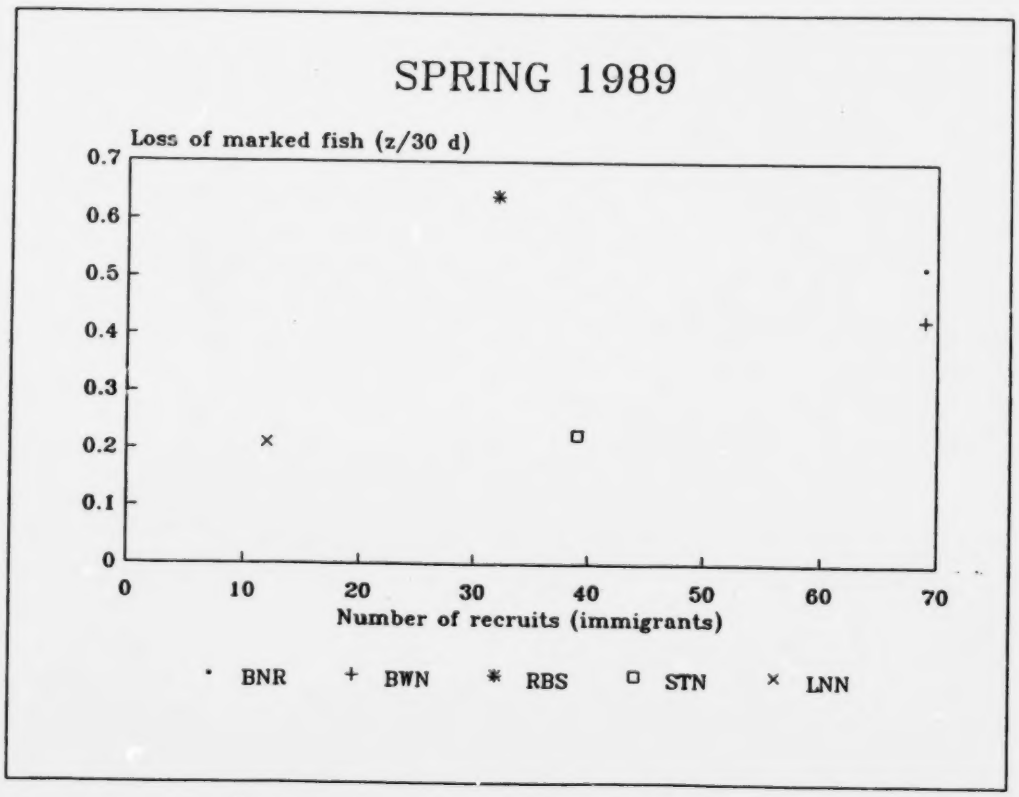


Figure 79. Instantaneous loss rates of marked brook trout and numbers of unmarked trout immigrating into study sections of the 5 streams. Both spring and fall data are shown.

Stone Run is out of place with respect to ranking of episode severity; toxic events occurred during spring 1989 yet trout density remained quite high.

Despite our manipulation of these populations and episodes of varying severity, populations tended to be fairly stable. Apparently wild brook trout are able to cope with toxic events. At this point the most plausible explanation we can offer is that availability of refugia allows trout to survive these episodes. This is based on observations made from telemetry studies and on the distribution of trout in Linn Run. The high density of trout in Stone Run may be related to refuge availability.

Besides refuge availability, reproductive success of brook trout in the vicinity of the study sections may also be important in determining population densities. For example, low trout densities in Linn Run could simply be a function of reproductive success, which would be influenced by the availability of spawning sites, numbers of adults, flow regimes during incubation, and toxicity of stream water during incubation and soon after emergence. We are currently exploring this hypothesis.

BENTHIC MACROINVERTEBRATES

A one-year seasonal analysis of the composition of the benthic macroinvertebrate communities of Baldwin Creek, and Linn, Benner, Stone, and Roberts Runs has been completed. The purpose of this study was to document any changes in community structure which can be attributed to intermittent acidification. The study area in each stream is located between the water quality monitoring site and a point 300m upstream. Similar riffle habitats within each study area have been sampled in August and November of 1988 and February and May of 1989.

In the southwest streams, major differences exist in macroinvertebrate taxonomic composition and standing crop. The control stream, Baldwin Creek, exhibited a more diverse community and higher standing crop than did Linn Run. Total number of families represented in Baldwin Run ranged from a summer low of 12 to a fall high of 20 compared with a spring low of 7 and a fall high of 14 in Linn Run (Figure 80). The spring low in Linn Run coincides with a time when acidification is generally most severe while the fall peak approximates baseflow. Total number of families collected in Baldwin Creek was also greater than the total from Linn Run (Figure 81). The fauna of Linn Run was dominated by acid-tolerant forms including isopods and members of the stonefly family, Leuctridae. The three Ephemeropteran families were represented by a single individual suggesting drift as their origin and not a resident population. Standing crops were higher in Baldwin Creek on a seasonal basis (Figure 82) and nearly 2.5 times those of Linn Run when viewed annually (Figure 83).

Macroinvertebrate communities of the northcentral streams, which are characterized by less severe water quality fluctuations than those of the Laurel Hill, were less impacted. With the exception of the summer value in Benner Run (control), seasonal and annual standing crops were not markedly different among the three streams (Figures 82 and 83). Taxonomic composition of the benthic communities was also similar (Figure 80 and 81). Ephemeroptera, Plecoptera, and Trichoptera were well represented in each stream.

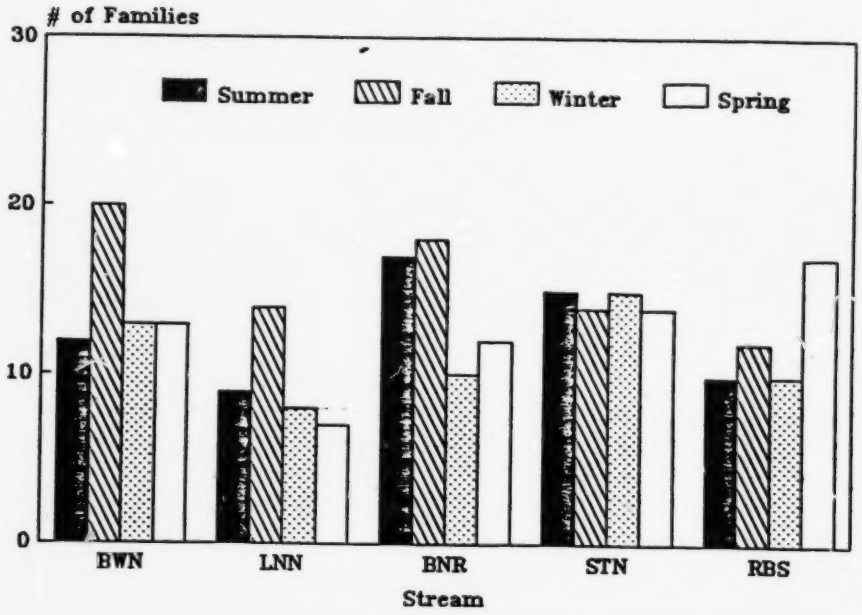


Figure 80. Seasonal comparison of macroinvertebrate taxa by family in study streams.

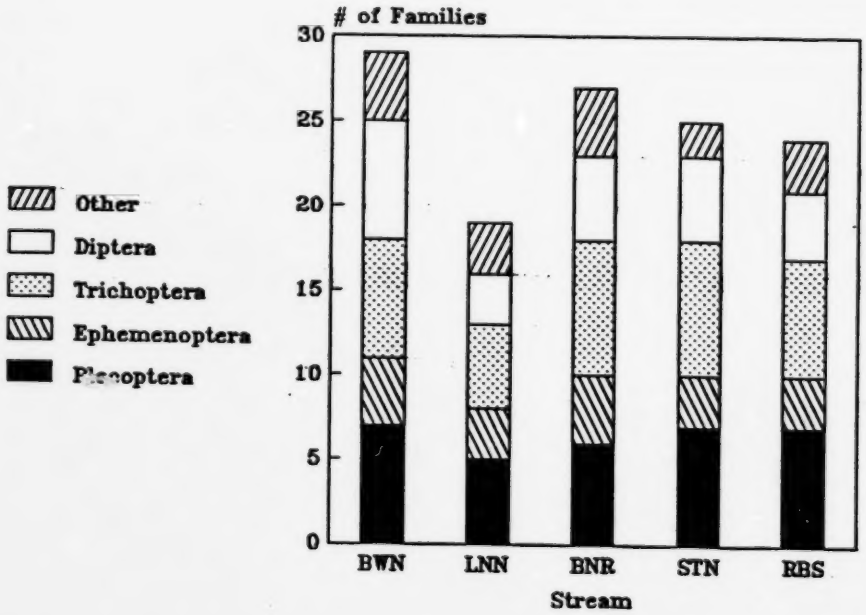


Figure 81. Comparison of macroinvertebrate families in selected orders for the study streams.

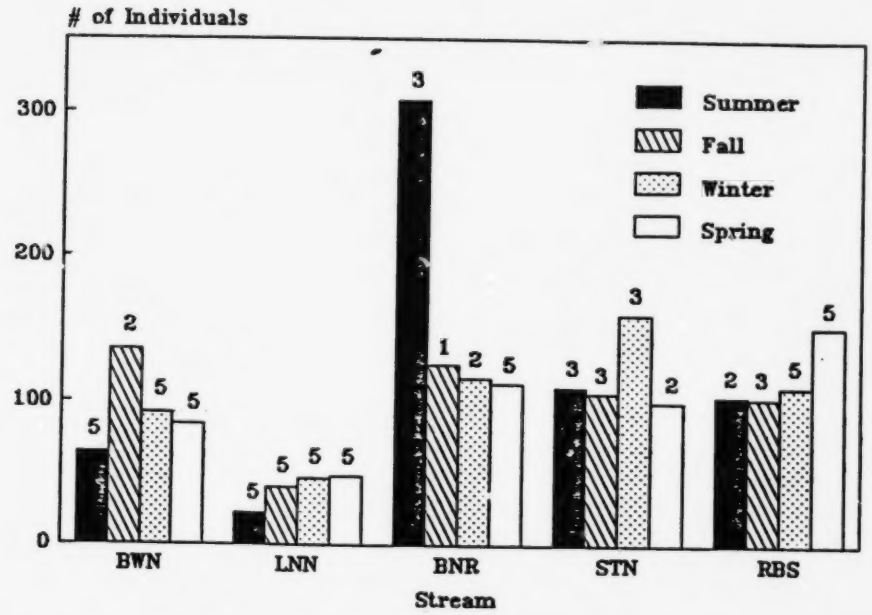


Figure 82. Seasonal comparison of macroinvertebrate standing crops in study streams. Numbers above bars indicate number of replicate samples.

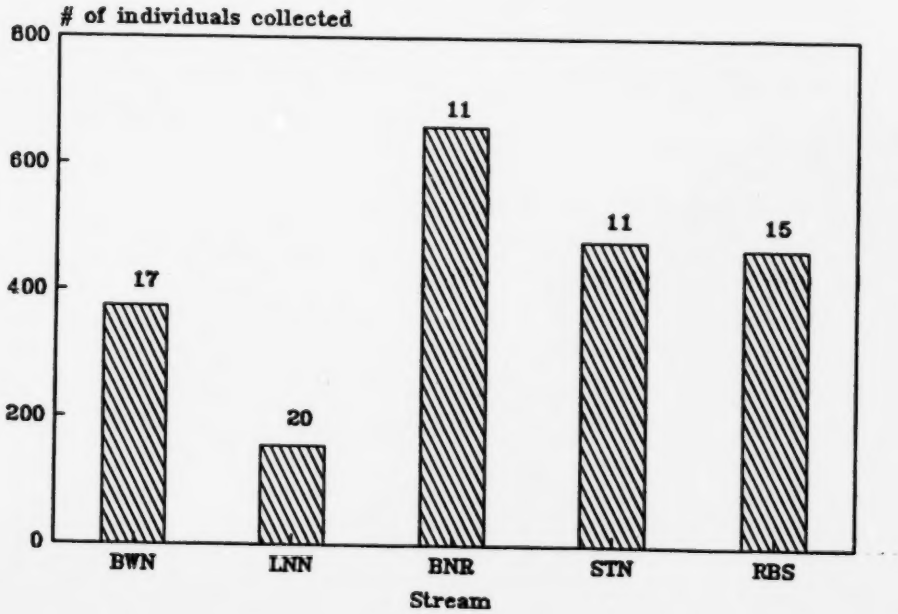


Figure 83. Total numbers of macroinvertebrates collected in study streams. Numbers above bars indicate number of replicate samples.

A one-year seasonal analysis of benthic macroinvertebrate communities from the 5 streams selected for the ERP reveals two extremes of response to intermittent acidification - severe perturbation (Linn Run) to little or no effect (Roberts Run and Stone Run).

CONCLUSIONS AND FUTURE PLANS

Preliminary findings presented in this report will eventually be supplemented with data from another year of monitoring and much more intensive data analysis. However, even after just one year of data gathering some major points seem clear.

Precipitation amounts for the first eight months of the project were average to slightly above average. The first winter was quite unusual in that no significant snowpack accumulations and no major snowmelt events occurred. Precipitation amounts were highest at the Linn Run site. Even adjacent basins experienced, at times, markedly different storm rainfall amounts.

Watershed hydrology varied considerably among basins, although the differences were subtle. Linn Run basin indicated greater response to precipitation than the other catchments. Baldwin Creek showed the most subdued response to precipitation, but when flows did increase they remained high for longer periods than on other basins. Separation of hydrographs into old and new water components using oxygen-18 has not been completed yet, but is expected to reveal any major differences in flow paths among basins.

Stream chemistry data show that pH, ANC, and aluminum concentrations are highly correlated with flow rates. Concentrations of DOC, sulfate, nitrate and cations are less correlated with flow and the correlation seems to vary from storm to storm. Inorganic monomeric Al dominates the total dissolved Al concentrations, thus the latter is a good index to biologically relevant Al content of stream water. During baseflow, calcium is the dominant cation and sulfate is the dominant anion in these streams.

Results show that episodes of low pH and elevated Al concentration can have dramatic effects on fish. Acidic episodes can result in conditions that are toxic to native species. Caged fish bioassays may overestimate the risk of mortality to free-ranging fish. The radio-tracking experiment showed that fish benefit from the presence of refuges with good water quality during episodes. However, refuges did not protect the entire fish population during the most severe acid runoff episodes. Densities of brook trout in headwater streams of the northern Appalachian Plateau appear to be influenced by both episode severity and refuge availability. Methods for characterizing episode severity and refuge availability need to be developed.

Benthic macroinvertebrate populations were influenced by water quality on the most severely acidified streams. Total number of families represented and total number of individuals were lower on Linn Run than the other four streams. Numbers of families and individuals were not markedly different among northcentral streams showing less-severe episodic acidification.

Future monitoring will include two additional intensive biological research periods; Fall 1989 and Spring 1990. Spawning surveys and measurements of reproductive success in each stream using VIBER boxes will be added in Fall 1989 in place of the restocking experiments. At least 10 additional storm events should also be monitored for complete chemistry on each stream, including episodes during the intensive periods. Snowmelt lysimeters will be in place to monitor the snowmelt rates and chemistry of meltwater released from the snowpack during Winter 1989-90.

ACKNOWLEDGMENT

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